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THE CHEMICAL NEWS, AUGUST 29, 1919

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THE
CHEMICAL NEWS

AND

JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

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JAMES H. GARDINER, F.C.S.

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THE CHEMICAL NEWS.

VOLUME CXVIII.

EDITED BY SIR WILLIAM CROOKES, O.M., D.Sc., F.R.S., &c.

No. 3064.—JANUARY 3, 1919.

THE PREPARATION OF ORGANIC STANNO- AND STANNI-CHLORIDES.

PART I.—SALTS OF THE ALIPHATIC AMINES.

By J. G. F. DRUCE, B.Sc.

THE only reference in the literature to double haloids of tin and aliphatic amines that has been traced is a paper by Cook (*Am. Chem. Journ.*, 1899, xxii., 435), in which the preparation and analyses of the double salts of stannous and stannic bromides and chlorides with the corresponding haloids of the methylamines and ethyl- and triethylamines are described.

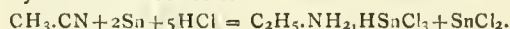
The double salts obtained with stannous chloride he terms chlorostannites, and similarly those derived from stannic chloride he refers to as chlorostannates. In order to indicate the molecular proportions of amine and metal numerical ratios are prefixed; thus, the substance $2(\text{CH}_3)_2\text{NH} \cdot \text{SnCl}_4 \cdot 2\text{HCl}$ is described as 2:1-dimethylamine chlorostannate. It was thought to be more convenient to regard the salts containing bivalent tin as stannochlorides and those containing quadrivalent tin as stannichlorides. The former compounds may be considered the salts of the (unknown) acid, H_2SnCl_4 or HSnCl_3 , and the latter as salts of the acid H_2SnCl_6 . Engels (*Comptes Rendus*, 1886, ciii., 213) has isolated the latter acid with six molecules of water of crystallisation, analogous to chloroplatinic acid, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$. But no acid derived from stannous chloride appears to have been prepared, although from conductivity experiments S. W. Young (*Journ. Am. Chem. Soc.*, 1901, xxiii., 21) inclines to the opinion that HSnCl_3 or H_2SnCl_4 exists in solution.

The amine stannichlorides are analogous to the platinichlorides; thus, methylamine stannichloride, $(\text{CH}_3\text{NH}_2)_2 \cdot \text{H}_2\text{SnCl}_6$, is analogous to the platinichloride, $(\text{CH}_3\text{NH}_2)_2 \cdot \text{H}_2\text{PtCl}_6$.

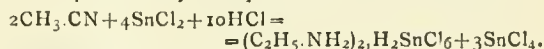
Cook (*loc. cit.*) prepared the aliphatic amine stannochlorides by mixing solutions of the amine hydrochloride and stannous chloride. The stannichlorides were similarly obtained, using solutions of stannic chloride. His preparations have been successfully repeated, and in addition the diethylamine salts have been isolated and examined.

Methylamine stannochloride was also produced by the reduction of hydrogen cyanide with tin and hydrochloric acid, and the stannichloride has resulted from the reduction with stannous chloride, but in neither case was the reaction quantitative. The melting points and composition of the salts prepared in this way were identical with those obtained from the amine hydrochloride and the chlorides of tin. The reduction of nitriles by tin or stannous chloride and hydrochloric acid with the forma-

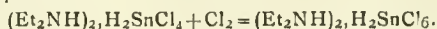
tion of the double salts of the resulting amines appears to constitute a general reaction. Thus it has been found possible to prepare the stannochlorides of methylamine, ethylamine, and certain other amines with an aromatic nucleus by the reduction of the corresponding nitriles with metallic tin. The reaction is expressed by the following typical equation for the conversion of acetonitrile into ethylamine stannochloride:—



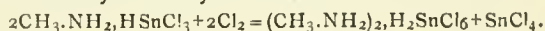
With stannous chloride the nitriles yield stannichlorides as is represented by the equation:—



Stannochlorides can frequently be converted into the stannichlorides by chlorination, either by slowly passing the gas into a solution of the stannochloride in dilute hydrochloric acid or by slowly adding chlorine water to a concentrated solution of the salt of bivalent tin. In some cases addition of chlorine only is evolved, as, for instance, with the diethylamine salts. The change may be expressed:—



But in other cases the reaction is a little more complex, and afterwards a portion of the tin in solution is present as uncombined stannic chloride. An illustration of this is afforded by the methylamine salts:—



Consequently, in the conversion of salts of the type BH_2SnCl_3 into stannichlorides $\text{B}_2\text{H}_2\text{SnCl}_6$, when oxidation was complete (which was ascertained by withdrawing a few drops of the solution and adding mercuric chloride) solution which gives a precipitate with stannous compounds, a quantity of amine sufficient to combine with the free stannic chloride was added in most experiments. As might be expected this addition doubled the yield of stannichloride.

Methylamine Stannochloride, $\text{CH}_3 \cdot \text{NH}_2 \cdot \text{HSnCl}_3$.

Methylamine hydrochloride (2.25 grms.) and crystalline stannous chloride (7.23 grms.) were dissolved together in 80 cc. of dilute hydrochloric acid (one part of concentrated acid to three parts of water). The solution was concentrated slightly on a water-bath, and on cooling deposited a mass of hair-like silky crystals, which were filtered off, washed with a little cold dilute hydrochloric acid, drained, and dried on a porous plate. This salt was much less soluble in water and dilute acid than either of the constituent chlorides. It did not melt when heated to a temperature of 305° .

When twice the above proportion of amine hydrochloride was used the crystals formed were identical with those prepared from the constituent salts in the molecular ratio 1:1.

Methylamine stannochloride has also been obtained by reducing 1 gm. of hydrocyanic acid with 10 grms. of tin and 100 cc. of concentrated hydrochloric acid diluted with 50 cc. of water in a round flask fitted with a reflux condenser. The contents of the flask were gently warmed until the tin had completely dissolved. On cooling, a small crop of crystals (about 0.8 gm.) separated out, and were found to be identical with those described above. A second crop was obtained by concentrating the mother-liquor, but was found to be less pure.

When some of this salt was warmed with caustic soda solution an inflammable and alkaline gas was evolved (methylamine). On analysis—

0.4732 gm. gave 0.7906 gm. AgCl; Cl=41.34 per cent.

0.3035 gm. gave 0.1777 gm. SnO₂; Sn=46.14 per cent.

CH₃NH₂.HSnCl₃ requires Cl=41.35 and Sn=46.42 per cent.

Methylamine Stannichloride, (CH₃NH₂)₂.H₂SnCl₆.

Five grms. of the above stannochloride were dissolved in 50 cc. of dilute hydrochloric acid, and chlorine was slowly passed in for two hours, when the solution no longer gave a precipitate with a solution of mercuric chloride. It was concentrated on a water-bath and deposited crystals on cooling. These were collected and dried between sheets of bibulous paper. On heating they began to darken at 208°, but did not actually melt up to 305°. They dissolved in cold water to a clear solution which hydrolysed on keeping. If the aqueous solution was warmed immediate hydrolysis ensued.

This salt has also been obtained from methylamine hydrochloride (2.65 grms.) and crystalline stannic chloride, SnCl₄.5H₂O (7 grms.), which were dissolved together in 80 cc. of dilute hydrochloric acid by warming. The solution was concentrated a little, and on cooling it deposited crystals possessing the same properties and composition as those prepared by the other methods.

For the preparation of the salt from hydrogen cyanide a solution containing 0.6 gm. of this was treated with 9 grms. of stannous chloride dissolved in 80 cc. of dilute hydrochloric acid. The mixture was warmed in a flask fitted with a reflux condenser for an hour. The solution was then transferred to a basin and concentrated on a water-bath. When cooled the concentrated solution deposited crystals of methylamine stannichloride. On analysis—

0.5772 gm. gave 0.2213 gm. SnO₂; Sn=30.20 per cent.

0.2309 gm. gave 0.5001 gm. AgCl; Cl=53.60 per cent.

(CH₃NH₂)₂.H₂SnCl₆ requires Sn=30.05 and Cl=53.72 per cent.

Ethylamine Stannochloride, C₂H₅NH₂.HSnCl₃.

Ethylamine hydrochloride (2 grms.) and stannous chloride (5 grms.) were dissolved by warming with 50 cc. of dilute hydrochloric acid, and on slightly concentrating the solution and allowing it to cool long colourless needles separated. When heated they melted at 149°; they dissolved in dilute acids to clear solutions, but in water the salt was slightly hydrolysed.

Crystals, identical with the above in composition and properties and having the same m.p., were obtained by warming acetonitrile (1.25 grms.) with tin (7 grms.) and concentrated hydrochloric acid (50 cc.) until the metal had dissolved. On analysis—

0.3125 gm. gave 0.1886 gm. SnO₂; Sn=43.62 per cent.

0.5143 gm. gave 0.8171 gm. AgCl; Cl=39.29 per cent.

C₂H₅NH₂.HSnCl₃ requires Sn=43.77 and Cl=39.29 per cent.

Ethylamine Stannichloride, (C₂H₅NH₂)₂.H₂SnCl₆.

Five grms. of the stannochloride, dissolved in 50 cc. of dilute hydrochloric acid, were submitted to the action of a slow stream of chlorine for an hour. Small crystals of the stannichloride, melting at 180°, separated out after concentration and cooling.

When 7 grms. of stannic chloride and 1.6 grms. of ethylamine hydrochloride were dissolved in 60 cc. of dilute hydrochloric acid the solution yielded about 5 grms. of crystals identical with the above in composition, appearance, and melting-point.

The same salt has also been obtained by warming a gm. of acetonitrile with 10 grms. of stannous chloride in 30 cc. of concentrated hydrochloric acid diluted with an equal volume of water. When a clear solution was obtained it was cooled and deposited characteristic hard transparent octahedral crystals of ethylamine stannichloride. On analysis—

0.5559 gm. gave 0.1991 gm. SnO₂; Sn=28.21 per cent.

0.2572 gm. gave 0.5216 gm. AgCl; Cl=50.19 per cent.

(C₂H₅NH₂)₂.H₂SnCl₆ requires Sn=28.02 and Cl=50.22 per cent.

Dimethylamine Stannochloride, (CH₃)₂NH.HSnCl₃.

This salt was prepared by crystallising solutions containing 2 grms. of the amine hydrochloride and 5.5 grms. of stannous chloride. The needle crystals were almost colourless (very faintly yellow) and transparent, and melted at 197°. When the constituent haloids were mixed in different proportions the same salt was isolated on crystallisation. On analysis—

0.3140 gm. gave 0.1756 gm. SnO₂; Sn=44.05 per cent.

0.1153 gm. gave 0.1816 gm. AgCl; Cl=38.98 per cent.

(CH₃)₂NH.HSnCl₃ requires Sn=43.77 and Cl=39.29 per cent.

Dimethylamine Stannichloride, (Me₂NH)₂.H₂SnCl₆.

Chlorine water was added slowly from a burette into 25 cc. of dilute hydrochloric acid containing 5 grms. of the above stannochloride, until the solution no longer gave a precipitate with mercuric chloride solution. For this purpose 180 cc. of the chlorine water were required. Concentration to small bulk caused very pale pink almost colourless crystals to separate on cooling. The salt melted at 289°.

Similar crystals resulted from a hydrochloric acid solution (30 cc.) of 1.7 grms. of dimethylamine and 3.7 grms. of stannic chloride. On analysis—

0.2879 gm. gave 0.1020 gm. SnO₂; Sn=27.90 per cent.

0.2737 gm. gave 0.5539 gm. AgCl; Cl=50.06 per cent.

(Me₂NH)₂.H₂SnCl₆ requires Sn=28.02 and Cl=50.22 per cent.

Diethylamine Stannochloride, (Et₂NH)₂.H₂SnCl₆.

Diethylamine (3.65 grms.) and stannous chloride (5.65 grms.) were dissolved by warming together in 70 cc. of dilute hydrochloric acid and concentrating to about half bulk. The crystals which separated were deliquescent, and consequently were dried on a porous plate in a desiccator over solid sodium hydroxide. They melted at 58°. On analysis—

0.9852 grm. gave 0.3640 grm. SnO_2 ; $\text{Sn} = 29.11$ per cent.
0.5930 grm. gave 0.8355 grm. AgCl ; $\text{Cl} = 34.75$ per cent.
 $(\text{Et}_2\text{NH})_2\text{H}_2\text{SnCl}_4$ requires $\text{Sn} = 29.04$ and $\text{Cl} = 34.69$ per cent.

Diethylamine Stannichloride $(\text{Et}_2\text{NH})_2\text{H}_2\text{SnCl}_4$.

Four grms. of diethylamine stannochloride were dissolved in 50 cc. of dilute hydrochloric acid and treated with chlorine for one and a-half hours. Crystals were obtained on evaporation to small bulk, and were filtered off on a Büchner funnel at the pump, and finally dried on a porous plate in a desiccator as they were slightly deliquescent. They began to melt with decomposition at about 260° .

Long colourless transparent crystals of this salt, identical with those obtained above, have been prepared from 4.7 grms. of the base and 11.7 grms. of stannic chloride dissolved together in 100 cc. of dilute hydrochloric acid. They also began to melt and decompose at 260° . On analysis—

0.9805 grm. gave 0.3090 grm. SnO_2 ; $\text{Sn} = 24.83$ per cent.
0.1874 grm. gave 0.3375 grm. AgCl ; $\text{Cl} = 44.56$ per cent.
 $(\text{Et}_2\text{NH})_2\text{H}_2\text{SnCl}_6$ requires $\text{Sn} = 24.75$ and $\text{Cl} = 44.35$ per cent.

Trimethylamine Stannochloride, $(\text{CH}_3)_3\text{N}, \text{H}_2\text{SnCl}_3$.

Trimethylamine hydrochloride (1.9 grms.) and stannous chloride (4.5 grms.) were dissolved together in 60 cc. of hot dilute hydrochloric acid. On cooling fine white crystals, melting at $119-122^\circ$, separated. They only dissolved slowly in cold water, giving an acid solution which quickly hydrolysed when heated. On analysis—

0.5420 grm. gave 0.2852 grm. SnO_2 ; $\text{Sn} = 41.46$ per cent.
0.4104 grm. gave 0.6170 grm. AgCl ; $\text{Cl} = 37.22$ per cent.
 $(\text{CH}_3)_3\text{N}, \text{H}_2\text{SnCl}_3$ requires $\text{Sn} = 41.80$ and $\text{Cl} = 37.26$ per cent.

Trimethylamine Stannichloride, $(\text{Me}_3\text{N})_2\text{H}_2\text{SnCl}_6$.

The amine hydrochloride (1.9 grms.) and stannic chloride (3.5 grms.) were dissolved together in 60 cc. of dilute hydrochloric acid by warming. The solution deposited white flaky crystals, which were isolated. They did not melt below 300° , but showed signs of decomposition at that temperature.

This salt has also been prepared from the stannochloride by passing chlorine into a dilute hydrochloric acid solution (30 cc.) of 2 grms. of the stannous salt for an hour. On concentrating the resulting solution crystals of the stannichloride identical with the above were obtained. On analysis—

0.5244 grm. gave 0.1775 grm. SnO_2 ; $\text{Sn} = 26.67$ per cent.
0.2193 grm. gave 0.4151 grm. AgCl ; $\text{Cl} = 46.85$ per cent.
 $(\text{Me}_3\text{N})_2\text{H}_2\text{SnCl}_6$ requires $\text{Sn} = 26.39$ and $\text{Cl} = 47.09$ per cent.

Triethylamine Stannichloride, $(\text{Et}_3\text{N})_2\text{H}_2\text{SnCl}_6$.

The stannochloride of this base has not been isolated pure. Hydrochloric acid solutions containing amine and stannous chloride did not crystallise unless very concentrated, and the mass of crystals so obtained did not give satisfactory analytical results. In most cases the product undoubtedly contained some stannichloride since the precipitate with hydrogen sulphide was yellowish.

The stannichloride was prepared from 2 grms. of the base and 3.5 grms. of stannic chloride dissolved in 50 cc. of dilute hydrochloric acid, as colourless transparent short prisms easily soluble in cold water, producing a clear solution. It melted with decomposition at 268° .

When solutions of stannous and amine chlorides were left exposed to air for some days, or were submitted to the action of chlorine, they oxidised, and, on concentration, gave more or less impure crystals of the stannichloride. On analysis—

0.5799 grm. gave 0.1619 grm. SnO_2 ; $\text{Sn} = 21.98$ per cent.
0.3266 grm. gave 0.5355 grm. AgCl ; $\text{Cl} = 40.13$ per cent.
 $(\text{Et}_3\text{N})_2\text{H}_2\text{SnCl}_6$ requires $\text{Sn} = 22.33$ and $\text{Cl} = 39.86$ per cent.

A METHOD FOR DETERMINING THE COMPOSITION OF A MIXTURE OF SIMILAR SALTS OF TWO METALS, WITHOUT SEPARATING THE MIXTURE INTO ITS CONSTITUENTS.

By H. N. WILSON.

It is often necessary in analysis to find the quantities of two very similar metals in a mixture and in many cases the metals are difficult to separate, and the method to be employed is often expensive. In the first class may be placed mixtures of strontium and barium, or antimony and arsenic, and in the second mixtures of sodium and potassium. In all such cases an arithmetical method would be vastly useful and time saving.

Such a method has been discovered in the course of investigations on potassium, and it is proposed to show how it may be used to advantage in this and other cases.

For determining potassium apart from sodium without using perchloric acid or platinum tetrachloride it is first of all necessary to obtain a mixture of the chlorides free from impurity and then to estimate the percentage of chlorine. Then by the means shown below the two constituents may be calculated.

The atomic weights are:—K, 39.10; Na, 23.00; and Cl, 35.45. From these we know that pure potassium chloride contains 47.5519 per cent of chlorine, and sodium chloride 60.6501 per cent of chlorine.

These two cases (0.00 per cent NaCl and 100.00 per cent NaCl) may be taken as the limits of a mixture of the two salts, and so the limiting percentages of chlorine are respectively 47.5519 and 60.6501, as shown in the graph appended, which shows the rise in Cl as the sodium chloride increases.

It will thus be seen that while the percentage of chlorine rises 13.0982, the percentage of sodium chloride rises 100.00, so when the percentage of chlorine rises 1.00 the percentage of NaCl rises $\frac{100.00}{13.0982} = 7.6346$.

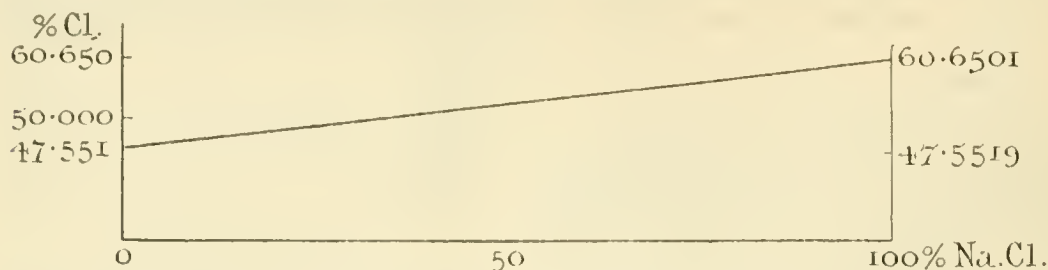
So if we subtract the minimum possible percentage of chlorine in the mixture from the percentage found in the sample under examination, and multiply the result by 7.6346 we obtain the exact percentage of sodium chloride in the mixture, and from this the percentage of potassium chloride or of metallic potassium can easily be obtained.

Example.—A given mixture of sodium and potassium chloride shows 50.5061 per cent Cl, how much potassium is present? Now, $50.5061 - 47.5519 = 2.9542$, and $2.9542 \times 7.6346 = 19.1491$, which is the percentage of sodium chloride in the mixture.

$\therefore$ The percentage of KCl is 80.8509.

$\therefore$ The percentage of metallic potassium is 43.3812.

A case in which the above method would be useful is in the determination of total alkali in flue dust; in this case the soluble portion would have to be extracted, and all other metals and sulphates precipitated by the usual means, which will give in solution a mixture of ammonium compounds, and K and Na salts which are broken down by heating into carbonates, &c., which dissolve in HCl to form chlorides, from which the estimation is easy.



Another case in point is the determination of barium in a mixture of calcium and barium carbonates. The carbon dioxide can be most easily determined; from it the barium can be found as follows:—In CaCO_3 is 43.994 per cent CO_2 , and in BaCO_3 is 22.234 per cent CO_2 , which is the lowest limit. By subtracting this from 43.994 we obtain 21.760; so if the percentage of carbon dioxide be diminished by 22.234 and the number so found multiplied by $\frac{100}{21.760} = 4.596$ we find the percentage of calcium carbonate in the mixture.

Enough has now been said to show the great use and adaptability of this method and also its time-saving properties. Numerous other cases will doubtless occur to the practical manipulator in his own branch, to which this short paper may be of use; if it is so, its purpose is accomplished; if not, the mathematical interest still remains.

THE BRITISH CHEMICAL - WARE MANUFACTURERS' ASSOCIATION.

THE following letter has been sent by the Joint Committee representing the Allied Associations to the Inter-Departmental Glass Trades Committee of the Ministry of Munitions, also the appropriate Government Departments. A separate case is being prepared for establishing on a secure basis in this country, on similar lines, the Porcelain Industry and Glassware for Lighting.

The Secretary,
INTER DEPARTMENTAL GLASS TRADES COMMITTEE,
22, Hertford Street, W.

SIR,—We desire on behalf of the following Associations, viz., the British Chemical Ware Manufacturers' Association, the British Flint Glass Manufacturers' Association, the British Lamp-blown Scientific Glassware Manufacturers' Association, and the British Laboratory Ware Association, to put forward for your careful consideration the very strong case for establishing on a secure basis in this country the key industry, or rather the "Master Key" industry:—"Scientific, Heat Resisting, and Chemical Glassware."

1. On the outbreak of war the country was faced with a very serious shortage of chemical glassware, the only sources of supply in most classes of articles being the stocks of enemy-made articles held by the merchants in this country; but for these stocks the situation would have been disastrous, as there were no existing facilities for manufacture.

2. The extreme seriousness of the situation has been acknowledged and has been referred to in both Lord Balfour of Burleigh's report and Dr. Addison's opening speech to the first meeting of the trade when the Whitley Inter-Industrial Committee was formed.

3. The absolute necessity of this industry to the country will be appreciated when once it has been realised that the development of all industries depends primarily on

the progress made in the laboratory, where new processes can be worked up and the means of utilising waste products can be discovered.

4. The following industries besides using glassware common to all laboratories, use special glass apparatus particularly adapted to their own needs, and if these were unobtainable or withheld, the result must at the very least be very damaging to the business concerned.

These industries include:—Agriculture, armament firms, breweries, cement manufacturers, chemical manufacturers, dyes, explosives factories, food production, gas companies, iron and steel works, leather and tanning industry, non-ferrous metal trades, oil cake manufacture, oil and tar distilleries, sugar manufacture, paper makers, &c. In addition to the laboratories for industrial purposes, there are all the medical and research laboratories attached to the hospitals, the county and municipal laboratories devoted to public health and hygiene, and last but by no means least the various laboratories at the universities, in colleges, schools, and technical institutes, private laboratories, &c., all of which use special glass apparatus, and are always wanting apparatus of new types. In fact, there is no branch of our national life, economic or social, which is independent of scientific and chemical glassware, and no other industry can lay claim to such indispensability. We therefore justify our claim to be the "Master Key" industry of the country.

5. This is the very industry which we desire to fortify, but owing to the war and the long period of training necessary to produce a skilled workman, we have not yet been able to get a sufficiency of labour trained to meet all demands made on us for scientific glassware.

6. It must be remembered that this is an industry which prior to the war was practically non-existent in this country, and consequently there was no labour skilled in the working of scientific glassware ready to step into the breach on the outbreak of war. It is true that there were a few glassworkers at the blowpipe who were available for training new and unskilled labour, but there was practically no skilled labour available for the manufacture of heat resisting glassware and other chemical apparatus. This labour had to be trained, and it speaks volumes for the trade that they have been able to do so much during the war; had it not been for the help of the Optical Munitions Glassware Department of the Ministry of Munitions in protecting our labour we should not have been able to record such advances as have been made.

7. We now look forward, with continued help, to establishing thoroughly on a secure footing this "Master Key" industry in this country. The progress which this country makes in industry after the war will depend to a very large extent on the increase and development of scientific control and scientific research into the by-products of manufacture, and it is unthinkable that all this should be dependent on foreign countries, through their laboratory glassware.

8. This industry will give employment to a large number of men and women, and indirectly on it depends ultimately the economic development of the country, as well from an industrial as from a public health standpoint.

9. It is very difficult to give figures to show that ours is an industry deserving of fostering, as there are no figures available of the pre-war conditions in this country (the industry having been monopolised by the Germans and Austrians).

10. To the best of our belief the conditions under which scientific glassware was manufactured abroad were such as would never be allowed to exist here. The workmen were often continually in debt to their employers, who owned their houses, the shops at which they dealt, and, in fact, the whole district in which they lived; the hours of labour were very long, the wages very low, and in many cases prison and child labour was employed, the result being "super dumping" at prices with which it would be impossible to compete.

11. The present wholesale prices of British-made glassware vary according to the quality and the make of the articles, and are from two to upwards of four times the pre-war price of the foreign-made articles, against which the facts stated above have to be borne in mind, as well as the advanced cost of wages, materials, &c., as the following table will show:—

Materials.	1914.	1915.	1918.
Soda ash.. ..	£3 0 0	£3 13 0	£7 0 0
" nitrate.. ..	10 0 0	10 10 0	24 0 0
Potassium nitrate..	22 0 0	43 0 0	51 0 0
Zinc oxide	—	49 0 0	89 0 0
Borax glass powder	22 0 0	56 0 0	103 0 0
Coke	13 0	1 5 0	2 1 8

Wages.	1915.	1915.
Glassblowers (at furnace)	£2 10 0	£5 10 6 Min. week
Stokers	1 18 0	4 0 0 "
Bricklayers	2 10 0	4 0 0 "
Labourers	1 12 0	3 0 0 Week
Boys	10 0	1 0 0 "
Girls.. ..	—	Doubled 1915 rate

These figures relate to the London district (Duroglass).

12. There are three principal reasons why the industry has not been able to prepare itself for "after the war" trade:—

- (1) The experimental work entailed in establishing the new industry has prevented the accumulation of funds;
- (2) In other cases the accumulation of funds has been prevented by the Excess Profits Duty;
- (3) The fact that the Government has insisted on all labour being concentrated on essential war orders, has prevented the training of labour for the more purely peace time class of work.

Some means must therefore be found to enable us so to strengthen our position as to ensure that this "Master Key" industry once established shall never leave the country.

13. In addition to the reasons stated above the following are further reasons why special treatment and consideration are necessary for the maintenance in this country of the chemical glass industry.

- (a) British glass making installations which have been erected since the war began will have cost up to three to four times what it cost Germany and Austria for similar installations erected and existing in pre-war times. Therefore the interest alone on the extra capital sunk in new British factories will represent a good profit to German and Austrian opponents before we can begin to make any profit at all. We therefore submit as below that Government assistance should be forthcoming in any approved case for the provision of new buildings and plant.
- (b) Generally speaking, labour costs (excluding non-productive labour and other charges) represent approximately 45 per cent of the total cost of chemical glass articles, and fuel more than a further 15

per cent; therefore the maintenance of the industry will depend upon measures being introduced to equalise the selling price in our Home Markets of goods produced in this country and those produced in other countries where cheap labour can be secured.

- (c) In some factories in this country Belgian labour has been employed, and as this must be repatriated after Belgium has been freed from occupation by the enemy, time should be granted for the adequate training of workmen to replace it. During the war it has not been possible to train lads, as immediately they have reached the age of eighteen and have acquired a certain amount of skill they have been withdrawn for military service.
- (d) Owing to the diversity of the demand for chemical, scientific, and medical glassware, every manufacturer has had to change continually from making one class of articles to another, thus preventing the adequate specialising necessary for the acquisition of high skill.
- (e) Many of the more difficult articles have not hitherto been attempted owing to lack of furnaces and labour.

14. British glass manufacturers must increase their existing plant to a very large extent before they will be in a position to meet the total requirements of the British Empire, and they are not only willing but extremely anxious to do so. This has been impossible during the war owing to the scarcity of building material and the lack of skilled labour, and also owing to the uncertain outlook for the industry in the future; the direct result of this is that the shortage of certain materials which could have been produced in these factories if they had been extended, has prevented the training of additional skilled labour in the lamp-blowing section of the industry.

For the reasons stated above we would respectfully petition the Government to consider and grant the following:—

1. That the importation of all chemical, scientific, and medical glassware, glass tubing and rod, be prohibited for a period of ten years after the termination of the war, subject to licenses being granted for the importation of such articles as are not manufactured in sufficient quantities or of satisfactory quality in this country. Such licenses only to be issued on the recommendation of the appropriate Government Department after consultation with and the acquiescence of the Associations signatory hereto.

2. That during the period of prohibition the prices that may be charged in this country be subject to general approval between the Government and the Associations concerned.

3. That after the expiration of the prohibition period, and in the case of any articles that may be imported forthwith under license as above, such a duty be imposed on importation as shall ensure that the makers of the foreign article, produced under conditions of cheap labour, preferential freight charges, or Government aid of any sort, shall not be in a better position than British manufacturers to compete in our home markets, and that the "anti-dumping" laws at present in force in America be put into operation in this country.

4. That prompt and generous Government assistance be granted towards the cost of providing forthwith new buildings and plant in any approved case.

5. That the Government take steps to safeguard the supply of raw materials required for the manufacture of chemical, medical, and scientific glassware.

6. That all Government departments, local authorities, State-aided institutions, schools, and colleges in receipt of Government or local grants, when purchasing supplies of chemical, medical, and scientific glassware, be compelled to indent exclusively for goods of British manufacture.

We, the Joint Committee appointed for the purpose of bringing these recommendations before you, beg to sign ourselves, Your obedient Servants,

DOUGLAS H. BAIRD, A. MARRIOTT POWELL. For the British Chemical Ware Manufacturers' Association (Glassware Section).

J. DONALDSON HARWARD, M. W. ZAMBRA. For the British Flint Glass Manufacturers' Association (Chemical Apparatus Section).

G. F. PRINCE. For the British Lamp-blown Scientific Glassware Manufacturers' Association.

C. A. MERCER, JOHN R. GRIFFIN. For the British Laboratory Ware Association (Glassware Section).

51, Lincoln's Inn Fields, London, W.C. 2.
November 4, 1918.

INTERNATIONAL INSTITUTE OF AGRICULTURE.

WITH regard to yield and consumption of the cereals and of other foodstuffs of prime necessity it may be fairly stated that almost all the really important countries have communicated their official estimates of crops in 1918 to the International Institute of Agriculture. This Institute is thus enabled to publish in its *Bulletin of Agricultural and Commercial Statistics* for November, 1918, these estimates in a very complete form, dealing with the world's food situation so far as the recent harvests are concerned.

We summarise in tabular form the aggregate results of the most important crops of foodstuffs, as harvested in those countries of the northern hemisphere which are mentioned in connection with each product.

It will be seen from these figures that, as compared with the preceding crop, this year's yields have been excellent for rye (131 per cent of that in 1917), linseed (122 per cent), and wheat (118 per cent), while they were good as regards sugar beet (107 per cent) and barley (109 per cent).

The crop of oats was slightly better than that of 1917 (102 per cent), while potatoes yielded decidedly less (89 per cent), and maize was even lower (87 per cent).

As compared with the average yield of the five years 1912 to 1916, the current year 1918 shows excellently for rye (136 per cent), oats (117 per cent), and barley (112 per cent), and is also good as regards wheat (107 per cent) and sugar beet (106 per cent), with an average outturn for maize (99 per cent). A falling off may be noticed for potatoes (96 per cent) and especially for linseed (85 per cent).

Among the new data published in the bulletin now under examination we find the yield of wheat in Ireland for 1918 (1,616,646 quintals, or 129.9 per cent of the yield in 1917 and 287.3 per cent of the average 1912 to 1916), in the Netherlands (1,312,740 quintals, or 125.8 and 87.5 per cent), and in Sweden (1,800,600 quintals, or 96.4 and 73.8 per cent), those of rye in the Netherlands (2,592,670 quintals, or 77.1 and 70.8 per cent), and in Sweden (6,515,000 quintals, or 182.2 and 107.4 per cent), those of barley in Ireland (1,868,072 quintals, or 109 and 120 per cent), and in Sweden (2,819,000 quintals, or 110.1 and 90.3 per cent), those of oats in Ireland (15,497,132 quintals, or 112.8 and 163.1 per cent), in the Netherlands (2,494,000 quintals, or 86.2 and 82.8 per cent), and in Sweden (9,389,000 quintals, or 96.3 and 77.2 per cent).

We may also mention the Italian maize crop (17 million quintals, or 88.7 per cent of the yield in 1917, and 71.2 per cent of the average), of the rice (5 million quintals, or 95.5 and 96.4 per cent), of the potato crop (12 million quintals, or 95.3 and 77.3 per cent), of hemp (800 thousand quintals, or 95.6 and 87.7 per cent), and of Italian wine (34 million hectolitres, or 71.3 and 88.3 per cent).

Production and countries.	Yield in 1918 thousands quintals.	Percentage of yield in 1918 as compared with—	
		1917	the average 1912-1916
		(1917=100).	(average=100).
<i>Wheat.</i> —Spain, England and Wales, Scotland, Ireland, Italy, Luxemburg, Netherlands, Sweden, Switzerland, Canada, United States, British India, Japan, Egypt, Tunis	545,118	118.1	107.1
<i>Rye.</i> —Spain, Italy, Luxemburg, Netherlands, Sweden, Switzerland, Canada, United States	40,782	131.5	136.0
<i>Barley.</i> —Spain, England and Wales, Scotland, Ireland, Italy, Luxemburg, Netherlands, Sweden, Switzerland, Canada, United States, Japan, Egypt, Tunis ..	129,156	109.5	112.4
<i>Oats.</i> —Spain, England and Wales, Scotland, Ireland, Italy, Luxemburg, Netherlands, Sweden, Switzerland, Canada, United States, Tunis	359,627	101.7	117.3
<i>Maize.</i> —Spain, Switzerland, Canada, United States	706,924	87.1	99.3
<i>Linseed.</i> —Italy, Canada, United States, British India	11,155	122.5	84.9
<i>Potatoes.</i> —France, England and Wales, Scotland, Italy, Luxemburg, Sweden, Canada, United States	294,159	88.9	96.0
<i>Sugar beet.</i> —Sweden, Canada, United States ..	66,775	106.8	106.4

With regard to the 1918-1919 crop in the southern hemisphere, where harvest is just beginning, the Institute is in possession of two forecasts of the yields of wheat. One from Australia for 22 million quintals represents 70.1 per cent of the yield in 1917-18, and 73.2 per cent of the average for five years 1912-13 to 1916-17. Another from the Union of South Africa for 2,594,535 quintals, or 107.9 and 154.4 per cent. Besides these, the information from Uruguay allows for the belief that there will be good crops of wheat, barley, oats, and linseed.

This *Bulletin* includes data relating to the number of live stock in Ireland, Canada, and New Zealand. In the two latter countries, but especially in Canada, we find a considerable increase in 1918 as compared with the previous year. Thus in the last mentioned country the number of milch cows has increased by 10.6 per cent, that of other cattle by 37.9 per cent, that of sheep by 28.2 per cent, and that of pigs by 18.5 per cent.

In the pages of the *Bulletin* that are dedicated to international trade in the cereals, we may call attention to information hitherto unpublished, and communicated by the Inter-allied Food Council, sitting in London, dealing with imports of cereals into France, Great Britain and Ireland, and Greece during the twelve months ending August 31, 1918.

Royal Institution.—The Christmas Lectures on "The Fish of the Sea," by Prof. D'Arcy W. Thompson, F.R.S., &c., will be continued on Saturday, Jan. 4, Tuesday, Jan. 7, Thursday, Jan. 9, and Saturday, Jan. 11, at 3 p.m.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, December 12, 1918.

Sir J. J. THOMSON, O.M., President, in the Chair.

The following papers were read:—

"Cooling and Evaporative Powers of the Atmosphere, as Determined by the Kata-thermometer." By LEONARD HILL, F.R.S., and HARGOOD ASH.

A further investigation has been made of cooling power of air at known temperature and velocity of movement in the large wind tunnels at the East London College, with the aid of Mr. N. A. V. Piercey, the lecturer on Aeronautical Engineering, timing the rate of cooling of the kata-thermometer, a large bulb spirit thermometer graduated between 100 and 95° F., and the factor of which was determined whereby the cooling power on a surface at body temperature is expressed in millicories per sq. cm. per sec. The formula was deduced $H = (0.27 + 0.49 \sqrt{v})\theta$ where θ = the difference between the temperature of the air and 36.5° C. Using this formula we found the velocity of the wind determined by the kata-thermometer at Kew Observatory agreed closely with the velocity determined by the Cup and Dines anemometers.

Using this formula to determine velocity, the cooling of the wet kata-thermometer was reinvestigated in a tube 3 in. in diameter, through which air was drawn from a chamber, the temperature and humidity of which could be varied. The formula was deduced $E(F-f)^{4/3} = 0.085 + 0.102 V^{0.3}$ for expressing the evaporative power, the full formula for the cooling of the wet kata-thermometer then being—

$$H = (0.27 + 0.49 \sqrt{v})\theta + (0.085 + 0.102 V^{0.3})(F - f)^{4/3}.$$

The effect on evaporative power of varying the temperature of the evaporating surface was determined, and the use of the kata-thermometer as a measure of evaporative power of drying processes pointed out. The effect of barometric pressure on cooling power was worked out in a chamber in which the atmospheric pressure was varied from +15 lbs. to 340 mm. Hg. The results were found to agree with the formula theoretically deduced—

$$H_1 = \frac{H_0}{2} \left(1 + \sqrt{\frac{p_1}{p_0}} \right)$$

where H_1 = cooling power at pressure p_1 , and H_0 = cooling power at atmospheric pressure p_0 .

The formula expresses influence of barometric pressure on convection cooling power. At ordinary temperatures cooling power exerted on dry kata-thermometer is half due to radiation, half to convection.

"Observations on Changes in the Blood Pressure and Blood Volume following Operations in Man." By H. C. BAZETT.

"The Four Visible Ingredients in Banded Bituminous Coal." By M. C. STOKES, D.Sc.

The coal discussed is the ordinary streaky bituminous coal of the British coal measures widely used in house and factory.

Disregarding for the time being the ultimate morphological nature of the plant organs contributing to them, four differing substances or constituents are described as composing such coal. These can be recognised by differences in their general character.

(a) Differences in their macroscopic appearance and texture (*i.e.*, with the naked eye in hand specimens).

(b) By their different behaviour when treated with various chemicals.

(c) By the differences in the *débris* of each which result from their treatment with various chemicals.

(d) By the differences in microscopic sections of untreated samples of each.

These differences are further followed up by analysis and distillations to be considered in a later paper.

Diagrams are given to show the characteristic distribution of these constituents in section, and to indicate if not a parallel to, at least a possibly useful comparison with, petrological work on rocks.

The four ingredients thus determined are *fusain* (the already widely discussed "mineral charcoal"), and *durain*, *clarain*, and *vitrain*, the three latter names being given now for the first time.

"On the Arc Spectrum of Scandium." By Sir W. CROOKES, O.M., F.R.S.

FARADAY SOCIETY.

The following resolution was passed on the motion of the President:—

That this Society, meeting during the week in which the crushing defeat of Germany was signalled by the armistice just signed, expresses the deepest gratitude to the Naval, Military, and Air Forces of the British Empire for the magnificent services they have rendered in bringing about the termination of hostilities.

GENERAL DISCUSSION ON "THE OCCLUSION OF GASES BY METALS."

The Ninetieth Ordinary Meeting of the Faraday Society was held on Tuesday, November 12, 1918, in the Rooms of the Chemical Society, Burlington House, London, W., when a General Discussion took place on "The Occlusion of Gases by Metals."

The Discussion was introduced by the President, Sir ROBERT HADFIELD, Bart., D.Sc., D.Met., F.R.S., who occupied the chair.

The President's address opened with an historical survey, beginning with the first scientific contribution on the subject made by Graham in 1866. Previously, Bessemer, in 1856, had recognised the importance of removing gases from fluid steel, and had patented a process to effect this. He outlined the work of later investigators as it concerns the ferrous metals, emphasising le Chatelier's views on the important influence of occluded oxygen on the structure of steel. He next reviewed Héroult's opinion as to the production of carbon monoxide in solidifying steel and its action in forming blow-holes, and he drew particular attention to the recent work of Allemann and Darlington, who by means of a gas-tight vacuum furnace capable of working at 1900° C., studied the gases occluded in ferrous alloys, and concluded that metals like aluminium, manganese, silicon, &c., acted as catalytic agents in preventing the occlusion of or in eliminating gases. The matter of sound steel castings was next considered and the difficulties of the early workers, who had no scientific guidance, were graphically illustrated. The great modern development of the use of silicon was due to the French metallurgists. The production of steel free from occluded gases, segregation, piping, and other defects, was of sufficient national importance as to call for a Special Committee to study it exhaustively.

The printed address concludes with a bibliography.

A short note by Mr. HENRY A. KENT indicated the wide field covered by the subject, which embraced all known actions and reactions.

He drew attention to some general considerations. Thus the base metals and alloys have a larger variation than the noble metals. The rare-earth metals occlude and combine at a low temperature, forming oxides, hydrides, nitrides, &c. The action of the accumulator depended on the absorption by lead of both oxygen and hydrogen.

Radio-active phenomena raised the question as to what might be the effect of occlusion of such gases as argon, helium, krypton, neon, and xenon.

Prof. ALFRED W. PORTER, D.Sc., F.R.S., opened the discussion with some "General Remarks on Occlusion of Gases in Metals."

The name "occlusion" was introduced by Thomas Graham in 1866 for the property of absorbing hydrogen and subsequently retaining it for an indefinite time, and has since been used to cover a multiplicity of phenomena of similar type. These phenomena can be grouped under the following heads:—

- i. Chemical combination of gas with metal.
- ii. Simple solid solution of gases.
- iii. Immiscible solid solution of gases in equilibrium with each other.
- iv. Solution accompanied by surface adsorption.
- v. Surface condensation under molecular forces unaccompanied by solution.
- vi. Inclusion.

It is usually a delicate matter to distinguish between these various types in practice. As an example, the question of the occlusion of hydrogen in palladium is discussed in some detail.

Amongst phenomena due to occlusion of gases may be mentioned the passivity of iron and the embrittling of iron. The Volta effect has often been attributed to condensed gases. Modern work has completely reopened the vexed question of Volta potential.

The embrittling of iron by occluded gases raised the question what constituted brittleness. Cobbler's wax was brittle to a sudden fracture. The question of time was involved.

Mr. COSMO JOHNS introduced the applied side of the subject in a paper "On the Physical Properties of Metals as affected by their 'Occluded Gases.'"

The word "occlusion" has been used to cover the many complex changes that take place when gases are absorbed by metals, and has thus become a general term rather than one which connotes a particular mode of association of gases and metals. While it may still be retained and used in that general sense, it seems desirable to distinguish as "Primary" such gases as were originally absorbed as such, and regard as "Secondary" such as are formed as the products of reactions that occurred during the cooling of the metallic mass.

The absorption of hydrogen by iron and copper under certain conditions are cited as examples of true occlusion, and the marked change in the physical properties of the two metals as described by Heyn is noted. As hydrogen is more soluble in the molten state of these metals than in the solid, it would follow that if the existence of a vitreous, or non-oriented, phase as an intercrystalline cement is admitted, the result of the cooling of a metallic mass containing hydrogen would be the concentration of the gas in the intercrystalline film, and the physical properties of the mass might be profoundly affected by a comparatively small quantity of gas.

The gaseous oxygen compounds found in iron and copper are more difficult to discuss, for in the case of iron it is certain that a portion of CO and CO₂ found in the solid metal is of secondary origin, formed during the cooling of the mass by reactions between dissolved iron oxide and carbon. If the mixed gases in the ratio that would be in equilibrium with the molten iron are soluble, then they would suffer concentration during cooling and would occur between the crystals. The SO₂ found in copper is probably partly secondary. It has been found that the value of the surface tension of liquid steel varies inversely as the quantity of occluded gases found in the solid metal. This is probably due to the effect of the dissolved iron oxide reducing the value of the surface tension, the occluded gases found being to a considerable extent oxygen compounds of secondary origin. From observations made on copper it appears probable that the same rule applies, but the evidence was not conclusive, and it is very desirable that the experiments be repeated under better controlled conditions. It is concluded

that "as all of the metals used for industrial purposes contains gases as constituents, and as all the more complete physical investigations of the common metals have been made on specimens containing such gases, it follows that we have no knowledge of the physical properties which the pure metals or their alloys would possess if they could be produced, and such data as are available can only refer to metals or their alloys with an unknown quantity of gases as important constituents."

Captain J. W. MCBAIN (Bristol University) communicated a paper on "Theories of Occlusion; and the Sorption of Iodine by Carbon."

It was emphasised that sorption phenomena often include a number of independent factors, such as absorption (surface condensation), absorption (solid solution), and various types of chemical reaction. These differ greatly in the time relationships and quantities involved, as in their dependence upon temperature.

After drawing attention to striking theories of these phenomena which have been recently advanced, arising out of the study of the structure of crystals by means of X-rays, experimental results were described, involving iodine and carbon and exhibiting typical sorption behaviour. Some of these experiments had been allowed to proceed for periods up to eleven years.

Dr. ANDREW McCANCE (Glasgow) read a paper entitled "Balanced Reactions in Steel Manufacture."

The reactions which take place in a melting-furnace are mainly balanced reactions, in which the important influences are temperature and concentration of the reactants. During melting the steel is in contact with a variety of gases with which it may react, but the only reaction which conforms with the well-known practical fact that cold melted charges have a higher content of FeO in the slag on melting than those which have been worked at a higher temperature is the oxidation caused by the presence of steam: $-3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2$.

This reaction has a positive heat balance, and proceeds from right to left when the temperature is increased.

During boiling the carbon is removed according to the equation $\text{FeO} + \text{C} = \text{CO} + \text{Fe}$.

There are several reasons for believing that FeO is soluble in liquid steel, and as a consequence, in those charges which are worked with only one ore addition, the log carbon plotted against time should be a straight-line law. Experiment shows that this is so, and further that there is a distinct alteration in the rate at which the carbon is oxidised after boiling commences compared with the previous rate.

Along with this reaction another takes place, namely, $\text{FeO} + \text{CO} = \text{CO}_2 + \text{Fe}$, which is very important, and which accounts for the proportion of CO₂ found in the gases extracted from steel. Experimental evidence supports the view that this reaction is the controlling reaction for blow-hole formation. When there is a high content of CO₂ in the liquid steel, blow-holes are formed owing to the limited solubility which solid steel has for this gas. An excess of this gas is present when much FeO is also present—i.e., when the steel is highly oxidised. The action of deoxidants, by removing the FeO, at the same time converts the CO₂ into CO, for which the steel in the solid state has still a considerable solubility. So long as the saturation limit is not reached no blow-holes will be formed.

In estimating the gases contained in steel, great care must be used in interpreting the results obtained, since they are certainly modified by the effect of reactions taking place between the evolved gases and the solid steel.

Dr. W. ROSENHAIN, F.R.S., contrasted the absorption of gases by liquid metals with their solution in ordinary liquids, where solubility decreased with rising temperature. This pointed to the formation of compounds more stable at higher temperatures, but the way in which the cooling metal parted with its gas involved many points calling for investigation. If the gas remained in the metal

after solidification it was probably in the form of a solid solution, and the nature of such solutions suggested that the gas was held in the supposed amorphous under-cooled liquid films bounding the crystals. These films played an important part in determining the properties of the metal.

Touching on the absorption of carbon monoxide in iron, he ascribed the carbonisation of iron below the critical point to the diffusion of this gas.

Answering Prof. Porter, he said all liquids were brittle, and cobbler's wax was a liquid. He had evidence that a crystalline aggregate like steel became brittle when the viscosity of the inter-crystalline cement was altered.

Prof. C. V. BOYS, F.R.S., found the brittleness of cobbler's wax a conundrum. He referred to the remarkable solubility of gases in liquid silver.

Dr. THOMAS BAKER read a paper on "*The Occlusion of Gases in Steel.*"

The paper is a résumé of the results of an investigation into the nature and composition of the gases evolved from steel when heated *in vacuo*, and the relation, if any, which exists between the temperature and rate of evolution of the gases. Three types of steel were experimented with, in the cast condition, and also after having been subjected to mechanical treatment.

From these experiments it appears that the composition of the gas is practically the same throughout the series (49 to 55 per cent hydrogen and 40 to 45 per cent carbon monoxide), but that the quantity varies considerably. It is greatest in the case of solid steel in the "ingot" condition, and least in the case where it has been submitted to drastic mechanical treatment.

There appears to be, also, some relation between the critical points of the steel and the temperature of the maximum rate of evolution.

Whether the gases obtained by heating the steel *in vacuo* are the ones evolved from the steel, or are formed by interaction between those actually evolved, is a still unsolved problem.

Dr. W. H. HATFIELD, commenting on one of Mr. Johns' conclusions, said that steel metallurgists knew very well the actual amounts of gases occluded in metals and alloys, on which so much work had been done. There was a tendency to exaggerate the amount present, which was usually estimated by volume. He thought that the effect of adding silicon, manganese, or aluminium to steel was not to prevent the occlusion of gases, but to cause the gases to be retained on freezing.

Sir CHARLES PARSONS, F.R.S., speaking on the formation of diamonds, said it had been proved to be connected in some way with occluded gases. Coal gas or hydrogen at about 2 tons pressure produced a remarkable effect on molten cast iron; it appeared to permit the extremely rapid growth of graphite throughout the metal. There was some action between the hydrogen and graphite—we did not know what.

Dr. H. A. BUMSTEAD described the methods he had adopted to get rid of the last traces of absorbed gases in metals in a liquid-air vacuum. The presence of the layer was indicated by the amount and character of the delta rays emitted.

Dr. H. S. TAYLOR drew attention to the untrustworthiness of the data available for calculations of the kind made in Dr. McCance's paper.

Sir T. KIRKE ROSE spoke on the "*Occlusion of Oxygen in Silver.*"

Following up the remarks of Dr. Rosenbain, he said that the compounds, for example the oxide of silver, were formed because they were endothermic compounds. This was in accordance with le Chatelier's law—the higher the temperature the more oxygen was absorbed by the silver. As the temperature fell, however, the oxygen was not expelled until solidification, and then it all went off at once and a shower of metallic globules was thrown out. Hydrogen occluded in molten copper behaved similarly. He concluded with some remarks on brittleness.

Prof. H. E. ARMSTRONG, F.R.S., referring to the two views of occlusion that had been put forward, said he regarded dissolution as a chemical phenomenon. The compounds formed were incomplete conversions, excepting at some particular temperature. In the case of oxygen and silver, a definite oxide of silver was formed at a high temperature, when both elements must be regarded as being in different molecular forms having great affinity for one another. In the case of iron, carbonic oxide had a high affinity for it at some high temperature; hence the ease with which carbonic oxide passes through iron; and similarly in the other familiar cases of occlusion. The unexpected resolution of alcohol into aldehyde and hydrogen under the influence of copper follows from the affinity of the latter for hydrogen.

On Sir Charles Parsons' remarks he would repeat his heresy that graphite was not a form of carbon.

Dr. W. H. HATFIELD controverted the views of Dr. McCance that hydrogen was unlikely ever to be the cause of blow-hole formation in steel, seeing that 75 per cent of the gas from blow-holes was hydrogen.

Mr. E. H. RAYNER supported the view that an oxide of silver stable at a red heat, but not at a low heat, best explained the phenomena connected with the absorption of oxygen in silver.

Sir GEORGE BEILBY, F.R.S., illustrated an effect of occluded gases by reference to the dependence of the recrystallisation temperature of cold-worked gold on the presence of minute quantities of hydrogen.

Dr. R. E. SLADE explained that the sudden issue of gas from silver, even with slow cooling, was to be expected from the cooling curve of silver and silver oxide.

Captain L. AITCHISON adduced reasons against the view that carbon monoxide formed a compound with iron. He stated that the addition of a very small amount of ammonia increased the rapidity of absorption of carbon monoxide in the case-hardening of steel. This was contrary to the idea that the intercrystalline cement was concerned in the absorption of the gas. He was critical of the partial pressure theory of absorbed gases stated by Mr. Johns.

Mr. C. R. DARLING spoke of the effect of the absorption of gases on electric welding. The pickling of the iron rod cited as negative in an acid produced a defective weld, in an alkali a sound weld. Again, under certain circumstances the weld absorbed a large amount of nitrogen and was sometimes sound, sometimes brittle. These and other phenomena were most obscure and called for investigation.

Another curious observation was the apparent boiling and bubbling of antimony far below the true boiling-point.

Lieut. H. C. GREENWOOD drew attention to the formation of blisters on iron by the occlusion of hydrogen, perhaps caused by the reduction of entangled oxide.

The action of caustic soda liquor on steel at high temperatures was to increase its strength and reduce its impact figure, and the action was roughly proportioned to the strength of the alkali.

Dr. N. T. M. WILSMORE said that the decrease of gas solubility in ordinary solutions with rise of temperature was only true of water. Other solvents behaved in the way molten metals did in this respect.

Dr. A. G. P. GWYER spoke on occlusion by aluminium and its alloys. Some blisters in cast metal, which developed when it was rolled into sheet, contained from 1/10 to 1/2 of their volume of occluded gas, principally hydrogen, and also carbon dioxide, carbon monoxide, methane, nitrogen, and oxygen. It was noteworthy that hydrogen was the chief gas occluded by non-ferrous metals and alloys, and the matter called for further study.

Dr. J. A. HARKER, F.R.S., said that in determining the melting-point of silver he had found that when the metal was cooled in a reducing atmosphere a definite, clean halt in the cooling curve appeared, but if the atmosphere was oxidising no such definite point was noticeable.

Nearly all metals which absorbed oxygen gave at the

moment of melting a large emission of gas, accompanied by a greatly increased electric emission. The predominating sign of the current was positive, but it always changed over to negative at the moment of melting oxidisable metals like tin or brass.

Mr. P. PEAKMAN referred to the importance of occluded gas in cast iron.

The PRESIDENT, in referring to this matter, spoke of the great difficulties the old iron and steel foundries laboured under in getting sound castings before science came to their aid.

Dr. W. H. HATFIELD said that the high percentage of silicon normally present in cast iron enabled it to take care of the gases. No blow-holes should occur if over 0.3 or 0.4 per cent silicon were present.

Dr. H. BURNS, in a written communication, drew attention to the discrepancies between the results of different experimenters on the nature and quantities of occluded gases. One source of error was often caused by gas evolved from the heated apparatus used in the experiments, and this suggested direct electric heating of the metal as being the best method to employ. Methods of experimenting and of analysing the gases called for study before much progress could be made.

Dr. R. S. WILLOWS, in a written communication, touched on the subject as it concerned X-ray apparatus, and he indicated points on which information was needed before the highest possible vacua could be produced in such apparatus rapidly and efficiently.

Prof. A. W. PORTER, replying to the discussion, said the difficulty of understanding how a very small quantity of hydrogen could contribute such brittle qualities to any metal remained unsolved. Later he hoped to suggest an explanation.

Mr. COSMO JOHNS reiterated the desirability of making experiments to see whether strained or unstrained metals showed any preferential capacity for absorbing hydrogen.

It was important to realise that we knew nothing about the properties of pure metals and alloys. All the data available referred to commercial metals containing unknown quantities of gases.

Annual General Meeting, November 12, 1918.

The following Officers and Members of Council were elected:—

President—Sir Robert Hadfield, Bart., F.R.S.

Vice-Presidents.—W. R. Bousfield, K.C., F.R.S.; Prof. F. G. Donnan, F.R.S.; Dr. Eugene Haanel; Prof. A. K. Huntington; Dr. T. Martin Lowry, F.R.S.; Prof. Alfred W. Porter, F.R.S.

Treasurer—Robert L. Mond.

Council—G. S. Albright; W. R. Cooper; Dr. C. H. Desch; Dr. J. A. Harker, F.R.S.; Emil Hatschek; Cosmo Johns; Harold Moore; E. H. Rayner; Dr. George Senter; Cav. Magg. E. Stassano.

The Report of the Council states that a further grant of £190 was made during the past year in aid of the research on "The Setting and Disintegration of Salts and other Crystalline Substances," which was carried out under the auspices of a special Committee appointed by the Council.

The Society has been affiliated to the Conjoint Board of Scientific Societies, and is represented thereon by Mr. W. R. Cooper.

It is stated that no fewer than five members of the Organising Committee of the British Scientific Products Exhibition recently held at King's College, London, were members of the Society, while the Organising Secretary of the Exhibition was Mr. F. S. Spiers, Secretary and Editor of the Society.

The Report also refers to the important progress made in the experimental work of the Nitrogen Products Committee of the Ministry of Munitions. The Society was largely instrumental in bringing to the attention of the Government the importance of the nitrogen problem.

In his Presidential Address the President, Sir Robert

Hadfield, referred to the success which had attended the General Discussions which were a feature of the work of the Society. During his term of office—since just before the war—11 Symposia had been held: on "The Hardening of Metals," "The Transformation of Pure Iron," "The Corrosion of Metals," "Methods and Appliances for the Attainment of High Temperatures in the Laboratory," "Refractory Materials," "The Training and Work of the Chemical Engineer," "Osmotic Pressure," "Pyrometers and Pyrometry," "Electric Furnaces," "The Co-ordination of Scientific Publication," and "The Occlusion of Gases in Metals."

FEDERATION OF BRITISH INDUSTRIES.

THE Adjourned General Meeting was held at Connaught Rooms on Thursday, December 12, Sir VINCENT CAILLARD presiding, when the following resolutions were unanimously passed:—

Peace Aims.

The Federation of British Industries fully endorses the arguments which have been advanced in other quarters for compelling the enemy countries to make such reparation as is possible by paying the full cost of the War, on the grounds of abstract justice, as a preventive of future aggression, and as a warning to any nation which may ever be tempted to follow their example. They desire, however, to urge more particularly on His Majesty's Government the serious economic aspects of the question.

Unless the enemy countries pay the burden will have to be borne by this country in the form of immensely increased taxation for many years to come. This taxation, however ingeniously its original incidence may be devised, must, like all other taxations, fall ultimately upon the industry of the country and form an element in the cost of production. A great increase in the total cost of production can only have three possible results—an increase in the price of the product, a diminution in sales ending eventually in national bankruptcy, or a reduction in the remuneration received by all classes engaged in production.

The first will be impossible owing to the competition of the countries who have taken no part in the War or who have taken a lesser part than this country, and whose total cost of production will consequently be less; the second means national disaster; the third will mean that producers of all classes—employers and employed alike—will have to work harder and receive less than they have ever done before. Capital will be driven away from British enterprises to those of less heavily burdened countries, and both the creation of new industries and the development of those already in existence will be seriously restricted.

Under such circumstances the general standard of living would inevitably be reduced, and it is even probable that the total national wealth would prove insufficient to provide simultaneously for the war charges and for the important but costly reforms in housing, wages, and hours of labour now contemplated.

The Federation therefore desires to urge upon His Majesty's Government the absolute necessity of transferring the burden of the War to those nations which are solely responsible for its creation.

They feel, however, that as much of the damage and loss caused by the War must necessarily remain beyond any possibility of reparation, that they must define clearly those items which they consider can be dealt with. These are—

- i. All expenses incurred as a direct or indirect consequence of the War by the Allied Governments.
- ii. Complete compensation for any loss of Allied public property or of private property owned by Allied subjects, wherever situated, including shipping and invested capital, and for all damage to such property arising from the War.

- iii. Compensation for all personal injuries, including a sum representing the capitalised cost of all pensions paid to disabled men and to widows and orphans.
- iv. An estimated sum to cover the loss in national power of production caused by the death or disablement of potential producers, and by the disorganisation of the means of production and transport.
- v. All enemy debts and obligations on whatever account.
- vi. Interest on all these charges from the date incurred until the date of final payment.

If the enemy Powers are unable, as is possible, to meet this debt by an immediate capital payment, its collection will probably extend over a considerable period.

During this period it will be necessary to provide some means of enforcing continued payment and of preventing attempted evasion by real and simulated transfer of allegiance to other countries, or by other political manipulation, and above all to provide adequate safeguards against any sudden and treacherous attack until there is a definite assurance of a genuine and enduring change of political theory and practice upon the part of our principal enemies.

Prolonged military occupation of any considerable portion of enemy territory would be very burdensome to the Allies by withdrawing a large number of men from productive employment, even if the actual cost of such occupation were borne by the enemy countries, while it might well impede the development of any stable and responsible democratic authority in the territory occupied.

The Federation would suggest that the necessary safeguards might be provided with the minimum of interference with the free internal development, economic, social, and political, of the defeated nations, and the minimum of expense to the Allies by assessing an adequate minimum annual sum to be furnished by the enemy countries, and by placing specific revenues calculated to produce this sum at the disposal of an inter-Allied Commission.

This Commission would be responsible for receiving this revenue and for paying the various Allies by instalments proportionate to the total amount owed to each Ally.

Should the specific revenues allocated for the purpose prove insufficient to produce the annual sum required, the enemy Governments should assign further revenue to the required amount.

Payment in kind, either by raw materials or in the form of replacement of property damaged or destroyed should only be permitted under safeguards which would effectually prevent any possible injury to the development of industry and employment in the Allied countries or any misrepresentation as to the value of such payments.

Payments in kind should therefore be made to the Inter-Allied Commission, which would dispose of the goods and credit the sums they received for them to the enemy Governments. The Commission should be empowered to refuse any manufactured articles which could be supplied by Allied countries.

The institution of such a Commission, if accompanied by a complete disarmament of the enemy forces, and by any necessary restriction on the development of aircraft or other means of sudden attack, would enable extensive military occupation to cease at an early date, and would probably enable the Allies, while occupying a few points of strategic importance from a military or naval point of view, to reduce their own armaments to an extent which would be impossible under any other conditions.

At the same time, by providing a common interest and responsibility, and a definite object for continued association and discussion, it should prove a valuable influence in constituting the Allies and Associated nations the nucleus of a League of Nations, into which the enemy countries themselves when their debt has been paid and

their period of atonement and probation completed, could in due course be admitted. Such a course would probably be preferred even in the enemy countries themselves to the constant interference and friction caused by a prolonged and extensive military occupation.

Trade Restrictions.—It has been necessary for the Government to control the prices and markets of certain commodities in the past, but where this has been done there has been an understanding that imports of these commodities from abroad should be prohibited. This has not been carried out in the case of cotton hosiery goods, as American cotton hosiery goods are now appearing in this country at a lower price than is possible for the British manufacturers. It was accordingly decided that urgent representations should be made to the Government requesting them in no case to remove the embargo on imports of these manufactured goods except after consultation with the Federation, who would approach the Association or Associations of the Trade concerned, and if necessary put them in direct touch with the Department.

Coal Supply.—"That the position of industry in regard to priority of Coal Supply is a serious menace to employment and the speedy conversion from War to Peace Production. And that the War Cabinet should take the matter into consideration immediately."

MISCELLANEOUS.

Disabled Soldiers. A duty devolves upon every one of us to do our utmost to find employment for those who have been disabled in the war. This remark should therefore be a direct appeal to all our readers to seriously consider if they cannot possibly find a job for at least one of our heroes. The Secretary of the Local War Pensions Committee will gladly answer inquiries and assist in finding a suitable man or men.

Award of the John Scott Legacy Medal and Premium.—The City of Philadelphia, acting on the recommendation of the Franklin Institute, recently awarded the John Scott Legacy Medal and Premium to Ernest J. Sweetland, of Upper Montclair, N.J., for the Sweetland Filter Press. This invention is to provide a self-dumping filter press, which will reduce to a minimum the labour involved in discharging the solid residue left in the press after filtration and also the labour of cleaning the press by hand.

Chemical Society Library.—With a view to meeting the growing demand for technical literature, the Council of the Chemical Society decided early in 1917 to increase the scope of the Library of the Society by a more liberal provision of suitable technical works and journals. It was also thought that by placing the existing library of 23,000 volumes, and the proposed extension at the disposal of other Societies and Associations, they might relieve themselves of the necessity of collecting and maintaining the literature relating to their special subjects and assist in the formation of a representative library of Chemical Literature, such as would be difficult to obtain by individual effort. A Conference of Representatives of Societies and Associations connected with Chemical Science and Industry was held to consider the means by which other Societies, &c., might co-operate in this extension, and financial assistance was subsequently offered by the following Societies, &c.:—Association of British Chemical Manufacturers, Biochemical Society, Faraday Society, Institute of Chemistry, Society of Dyers and Colourists, and Society of Public Analysts. Members of these contributing Societies, &c., will be permitted to consult the Library and borrow books from January 1, 1919. The hours of opening the Library will be as follows:—Mondays, Wednesdays, and Thursdays from 10 a.m. to 6 p.m., Tuesdays and Fridays from 10 a.m. to 9 p.m., Saturdays from 10 a.m. to 5 p.m.

The Ministry of Munitions announces that the suspension of the operation of Regulation 30a of the Defence of the Realm Act on acetic acid, grey acetate of lime, and acetone covers in addition products associated with acetone which have also been restricted under the Acetone Order, including methyl acetone, methyl-ethyl-ketone, and acetone oil. Trading in all of the above mentioned articles abroad as well as at home is now entirely free with the exception of those cases where export licenses have still to be obtained from the War Trade Department. No formalities are now necessary in connection with the import of these materials from America.

The Science of the Future.—Mr. A. A. Campbell Swinton, F.R.S., in his address as Chairman of the Council of the Society of Arts, delivered at the opening meeting of the Session on November 20, gives quite a hopeful forecast of scientific development in the near future. Great advance is to be expected in the application of wireless telegraphy as a means for diffusion of the world's news, and many suggestions are made for the utilisation of the more recent advances in thermoelectricity and kindred subjects. Mr. Swinton suggests that the devastation due to the war can in time be repaired, while the world store of scientific knowledge is "still intact"; this may be so, but the unfortunate devastation due to the war is not altogether confined to material property, which can of course be replaced; hundreds of our young men, with minds fully trained in scientific knowledge and method, have been sacrificed, and the world has suffered irreparable loss thereby. Mr. Swinton discusses the possibilities of the utilisation of radiant energy for industrial purposes at some length, and numerous suggestions are made in a manner characteristic of the author. The Royal Society of Arts is to be congratulated upon the energy of its chairman, under whose guidance a successful session may be confidently expected.

Waste Products.—The Munitions Inventions Department of the Ministry of Munitions has instituted inquiries with the object of ascertaining whether waste products of various chemical manufactures can be utilised for industrial purposes, and the Waste Products Committee of this Department has carried out experiments on the waste products set out below. Particulars as to the results of their experiments will be furnished to chemical manufacturers interested upon application being made to the Controller of Munitions Inventions, 10, Princes Street, Westminster, S.W. 1.

1. Sulphide of arsenic residues from the purification of sulphuric acid.
2. Residues containing appreciable quantities of selenium.
3. Waste hydrochloric acid from pickling.
4. Waste chromium sulphate liquors resulting from the oxidation of organic substances.
5. Residue from the manufacture of acetic anhydride.
6. Residues suitable for the purification of coal-gas from sulphuretted hydrogen.
7. Maize residues from the manufacture of butyl alcohol.
8. Chrome leather scrap.
9. Mimosa bark residues.

The Committee has also investigated various methods of derusting.

NOTES AND QUERIES.

Russian or Fish Glue.—I should be greatly obliged for a recipe for manufacturing Russian or fish glue in liquid form. What I really desire is a list of the various ingredients of which the glue is composed. I know, of course, that fish bones is one of the articles.—J. JOHNSON.

Manufacture of Bleaching Powder and Soda Ash.—A correspondent, possessing large quantities of carbonate of lime and having at command 3000 h.p. surplus electrical energy, wishes for particulars of an electrolytic process for manufacturing bleaching powder and soda ash.—Address, "Bleaching Powder," care of CHEMICAL NEWS Office.

ASSISTANT CHEMIST.—Wanted by Cocoa manufacturers for Analytical and Research work. University Graduate with experience in Food Analysis preferred.—Apply, stating age, qualifications, experience, and salary desired, to "Chemist," 25, Union Street, Bristol.

Chemist, University training and wide industrial experience, is now free to accept engagement as Chemist or Technical Adviser. Expert on Distillation Methods and Recovery of Volatile Solvents, &c. Late Chemist-in-charge of one of H.M. Factories. Ex-Army. Near London preferred.—Write to Box 46, Judd's, 97, Gresham Street, E.C. 2.

Chemist wanted, with first-class training and experience, for a Non ferrous Metals Laboratory (London), to organise and take charge, under Principal, of Laboratory employing two or three Juniors. Preference given to man with record for extremely accurate analysis (Inorganic) and successful Research Work.—Replies, in confidence, stating full experience, references, and salary expected, to "Chemist," care of Crossley and Co., Ltd., 57, Coleman Street, E.C. 2.

Chemist (46) desires Appointment, with Partnership or Financial Interest, with Agricultural or Analytical Chemist or Dairy Company.—Address, "C. 46," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Chemist (B.Sc., Lond.), Hons. in Chemistry, and with Continental training, seeks Appointment as Laboratory or Research Chemist.—Address, B. R., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Chemist (19), used to analysis of Ferrous and Non-ferrous Alloys, Steel-works, and general experience, seeks Situation.—Address, H. S., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Chemist (Hons. B.Sc. Chemistry), with Technical Analytical and Research experience, requires Post.—Address, S., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Metallurgist desires Position. Research work preferred. Public school and University Training. Experience in Metallography, Pyrometry, Heat Treatment, and Physical Testing of Aircraft and Automobile Steels.—Address, "Metallurgist," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Works Analytical Chemist required. One conversant with Soap Manufacture, Nicotine Extractions, and Agricultural and Horticultural Preparations. State full particulars and salary required.—Address, W. A., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Wanted, practical Chemist with Engineering knowledge and Pharmaceutical experience, scientific education, and acquainted with Analysis. State age, experience, and salary required.—Address, Duncan, Flockhart, and Co., 104, Holyrood Road, Edinburgh.

Youth, 19 (Lond. Matric.), requires Situation as Junior in Works Laboratory. Some experience in Public Analyst's Laboratory.—Address, "Peace," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

CHEMICAL LABORATORY FOR SALE by returned Prisoner. All pre-war material. Graduated glass flasks, &c., copper ovens, furnaces, bellows, blowpipe, physical balance (Kipps), 200 stoppered bottles containing chemicals, platinum utensils.—Address, Morison, 491, Fulham Palace Road, S.W. 6.

UNIVERSITY OF BIRMINGHAM. FACULTY OF SCIENCE.

PROFESSORSHIP OF CHEMISTRY.

The Council of the University invites applications for the CHAIR OF CHEMISTRY, vacant by the resignation of Professor PERCY F. FRANKLAND, F.R.S.

The stipend offered is £1000 per year. Applications may be accompanied by testimonials, references, or other credentials, and should be received by the undersigned on or before FEBRUARY 8th, 1919.

Further particulars may be obtained from—

GEO. H. MORLEY, Secretary.

THE CHEMICAL NEWS

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TRINITROTOLUENE RESIDUES AND THEIR UTILISATION.

"ISO-TROTYL," "LIQUID T.N.T." CHLORPICRIN,
AND SULPHIDE DYES.*

By MAURICE COPISAROW.

THE recent development of a great war industry—the manufacture of trinitrotoluene—has given rise to several problems, closely connected with one another, the most outstanding being:—

- (1) Conditions of nitration;
- (2) Methods of purification; and
- (3) Residues and their disposal.

The first two having been already dealt with by the author (CHEMICAL NEWS, 1915, cxii., 247, 283; 1916, cxiii., 37) it is intended now to deal with the problem of residues, which, owing to their gradual accumulation, require some method of utilisation.

The problems of residues, their recovery and disposal, can be regarded as part of the greater problem of the efficient and economical manufacture of trinitrotoluene. The residues are derived chiefly from two sources:—

- (1) Those accompanying in solution or suspension the used-up acids, and
- (2) Those obtained in the process of purification of trinitrotoluene by recrystallisation or washing.

The used-up acid is usually considerably diluted to precipitate as much as possible of the dissolved trinitrotoluene. This procedure when carried beyond certain limits must be regarded as wasteful, as, first, a portion of the nitro bodies remain invariably dissolved or suspended in the dilute acid, no matter what the dilution may be, and, secondly, the recovery of acid becomes a huge task involving the use of a large number of sulphuric acid concentrators.

A better method seems to be to dilute the acid just enough for the separation and convenient removal of the bulk of the nitro body and then to extract the used-up acid with toluene. This gives a fairly concentrated acid, practically free from nitro bodies, and a toluene extract, which is transferred into the nitrators. Leitch's English Patent 15,555, 1915, seems to be very much of this kind. The extraction of the nitro bodies with a solvent from the used-up acids is, of course, only necessary in case of acids to be concentrated or used for different purposes.

Whilst in the case of residues accompanying the used-up acid the problem is confined simply to their recovery, in case of residues derived from the purification processes the problem is their utilisation. Among the several methods of purification of crude T.N.T. the alcoholic treatment occupies an important position; the alcohol being applied either as a solvent and crystallising medium or as a washing agent for the crude T.N.T.

The latter method yielding a somewhat inferior product as compared with the former, gains much favour owing to the considerable technical advantage it presents, the more so as the purity of the product thus obtained answers all ordinary requirements.

On removing the alcohol from the mother-liquor in the first case and the washings in the second, a dark brown thick liquid is obtained.

This residue is slightly soluble in water, giving a

yellowish solution which, when treated with caustic soda, gives a red coloration characteristic of α -trinitrotoluene and some other nitro aromatic bodies accompanying it.

On prolonged distillation in a current of steam the distillate consists of a yellowish aqueous solution, no oil or solid matter being present, this indicating that the residue, whilst being to some extent volatile in steam, does not contain toluene or mononitro toluenes.

The percentage of volatile matter (alcohol, water, &c.) in the residue was determined by heating a weighed quantity of the residue in a shallow dish to constant weight at 97–99° C. and noting the loss in weight.

The matter insoluble in benzene (oxidation and condensation products of the polynitrotoluenes as well as inorganic matter) was determined by extracting a weighed quantity of the residue with twelve to fifteen times its weight of benzene, and noting the weight of solid residue. The quantitative nitrogen determination was carried out with samples carefully freed from volatile matter and matter insoluble in benzene; the benzene extract being freed from benzene and kept for ten hours at 97–98° C. The results obtained are as follows:—

Specific gravity of the residue ..	1.47	1.50 (20° C.)
Volatile matter	0.77	0.81 per cent
Matter insoluble in benzene ..	1.35	1.40 "
Percentage of nitrogen in a purified sample	15.95	16.01

Assuming the purified residue to consist of di- and trinitrotoluenes only (nitrogen in dinitrotoluenes, 15.4 per cent; nitrogen in trinitrotoluenes, 18.5 per cent), we find from the equation—

$$0.185x + 0.154(100 - x) = 15.95 \text{ (or } 16.01)$$

that the purified sample contains:—

Dinitrotoluenes	82.26	80.32 per cent
Trinitrotoluenes	17.74	19.68 "

The residue on long standing at the ordinary temperature gradually crystallises to a semi-solid mass, which can by means of a filter-press or centrifuge be separated into two parts:—

- (a) Brown solid containing 1.45–1.55 per cent matter insoluble in benzene, and (b) a liquid resembling the original residue.

The proportion of solid matter so obtained to the total varies appreciably, depending upon the conditions of the alcoholic treatment and the duration and range of cooling, but it is seldom below 18 per cent.

The author has investigated three methods of utilisation of the T.N.T. residues:—

- (1) As an explosive;
- (2) As various means of warfare; and
- (3) As dyes.

With the object of investigating the application of the residues and their products as explosives the following experiments were carried out:—

1. Nitrating the crude residue at 100–120° C. with a mixture of sulphuric and nitric acid containing 6 per cent H₂O and 15–17 per cent HNO₃, a light yellow opaque liquid (specific gravity, 1.49–1.51 at 20° C.) is obtained containing 48.4–64.5 per cent of trinitrotoluenes (nitrogen, 16.9–17.4 per cent), and forming a gelatinous mass with gun-cotton. Considering the high percentage of nitrogen and the property of dissolving gun-cotton this liquid must be regarded as a "liquid T.N.T." of a high standard suitable for the preparation of gelatinous dynamite to be favourably compared with the Nobel's explosive (D.R.P. 24235, 264503).

2. Nitrating in a manner described above a sample free from volatile and insoluble (in benzene) matter, the product is found to be practically identical as in No. 1. This method, whilst leading to a certain economy in acid, owing to diminished oxidation, involves much extra work.

3. Nitrating product from No. 1, 2, or the residue direct with a mixed acid containing 4 per cent H₂O and 17 per

* This paper, ready for publication early in 1916 and intended to follow directly the papers previously published (CHEMICAL NEWS, 1915, pp. 247, 283; 1916, p. 37), had to be kept back owing to war considerations.

cent HNO_3 at 120°C ., a slightly yellowish solid, resembling good quality crude trinitrotoluene, is obtained. Whilst setting at $57-58^\circ \text{C}$. the nitrogen determination of this substance indicates it to contain at least 98 per cent trinitrotoluenes ($\text{N} = 18.44$ per cent). Therefore this product must be regarded as a mixture of trinitrotoluene isomers. As to the actual state of the isomers in the product the fact that α -T.N.T. forms additive compounds in the solid state not only with hydrocarbons, phenols, and amines, but also with nitro-compounds, such as mono-nitro- and di-nitrotoluenes (Lepsius, *Chem. Zeit.*, 1896, xx., 839; Giua, *Ber.*, 1914, xlvii., 1718) suggests the possibility of the product consisting of a mixture of additive compounds rather than a mixture of free isomers (see "On the Theory of the Formation of Additive Molecular Compounds by Nitro-bodies," Pfeiffer, *Ann.*, 1916, 412, 253).

Noting the fact that α -, β -, and γ -trinitrotoluenes and probably all other modifications are practically of the same value as explosives (Will, *Ber.*, 1914, xlvii., 704), this low melting explosive, which may be conveniently termed "iso-trotyl," must be regarded as a useful and powerful constituent for blasting powders like bellite and robarite, and for war purposes, especially in cases where a lowering of the melting-point is required as in the case of trinitroxylenes.

4. The method of dissolving the residue in toluene, filtering, and then nitrating the filtrate in two or three stages is found to be unsatisfactory, as a portion of the nitrated product remains liquid (liquid similar to that described in No. 1 and 2), which is probably due to the fact that the dinitrotoluenes derived from *m*-mononitrotoluene are less readily nitrated than those formed from the *o*- and *p*-modifications, and also to the gradual weakening of the mixed acid as the nitration proceeds.

5. Submitting the solid and filtrate mentioned above to an exhaustive nitration it was found that both gave ultimately the same solid product setting at $57-58^\circ \text{C}$. as in No. 3.

The identity of the products of the nitration of the solid and filtrate and the fact that the nitration of the solid proceeds more readily, requiring less acid, suggest that the solid represents a higher stage of nitration than the filtrate, both leading ultimately on nitration to a mixture of isomeric trinitrotoluenes.

It appears therefore that—

1. No special purification of the residue, preliminary to further nitration, is to be recommended, as the slight excess of acid used up with the crude residue is more than compensated by the saving of extra work involved in the process of purification.

The matter insoluble in benzene present in the residue is only to a small extent transferred to the nitration product, the bulk of impurities being either oxidised or dissolved.

2. "Liquid T.N.T." prepared from the residue can be used with advantage for the preparation of gelatinous dynamite.

3. "Iso-trotyl" prepared from the residue can be usefully employed for blasting powders, or as a valuable ingredient for lowering the fusion point of explosives having a high melting-point.

4. Should both the "liquid T.N.T." and the "iso-trotyl" be in demand, the most economical way of preparing them would be to cool the crude residue, separate the solid, and then nitrate the solid to "iso-trotyl" and the filtrate to "liquid T.N.T."

Under the heading of utilisation for various means of warfare the author investigated the employment of the residues for the production of chlorpicrin, $\text{CCl}_3(\text{NO}_2)$. Applying Hofmann's method of preparing chlorpicrin, originally worked out for picric acid (*Ann.*, 1866, cxxxix., 111), i.e., the treatment of the nitro-body with bleaching powder, it was found that chlorpicrin could be obtained by treating the T.N.T. residues with bleaching powder; the yield compares favourably with that obtained by the

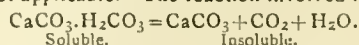
degradation of picric acid residues, allowing for the percentage of nitrogen.

The T.N.T. residues can be also usefully employed for the making of dyes. Fusing the residues or their nitration products with sodium sulphide, with or without the addition of sulphur, dyes are obtained which dye unmordanted cotton fast colours varying from grey to khaki and brown; the particular colour depending not only on the concentration of the dye-bath but also on the temperature and duration of fusion and the addition of sulphur. These methods of disposal of the T.N.T. residues, whilst in no way exhausting the methods of their possible utilisation, suffice to indicate that in the manufacture of trinitrotoluene there are no waste products in the actual sense of the word, as even the nitrous fumes so abundantly given off during the nitration can be easily recovered.

WATER SOFTENING.

By P. E. KING.

THE hardness in water is due to soluble salts of calcium and magnesium; "temporary hardness" to carbonates of lime and magnesia, held in solution by carbonic acid; "permanent hardness" to sulphates, nitrates, and chlorides of these metals, which are soluble of themselves. The greater part of the temporary hardness can be removed by boiling the water, but except in some cases where in de-oiling plants exhaust steam is used for this purpose this plan is not applicable. The reaction involved is:—



Soluble. Insoluble.

The carbonic acid gas holding the carbonate in solution is driven off, and the carbonate is thrown out of solution. The permanent hardness must be removed by chemical treatment; i.e., is not removed by boiling under ordinary atmospheric pressure. This distinction between temporary and permanent hardness fails altogether as soon as the water enters a boiler, for at the very high temperature of a boiler under high steaming pressure the calcium sulphate becomes insoluble and the magnesium chloride, inert while cold, becomes actively corrosive.

The methods of water softening may be divided into two distinct groups, the first of which can be sub-divided into three:—

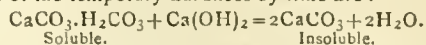
Group I., (a) the lime processes which is used in cases where the hardness is only temporary or mainly so.

(b) The soda process where either carbonate of soda or caustic soda is used.

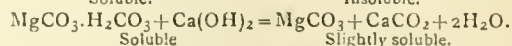
(c) The lime and soda process, which is the method in general use.

Group II.—In the second group is found the most recent method of softening water; i.e., the Permutit system:—

In Group I. the chemical reactions involved in the removal of the temporary hardness by lime are:—

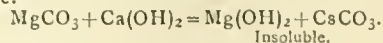


Soluble. Insoluble.



Soluble Slightly soluble.

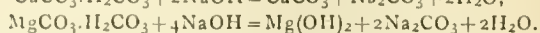
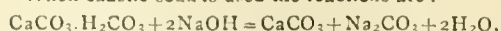
and with more lime the magnesium carbonate still in solution is converted into hydrate, which is practically insoluble.



Insoluble.

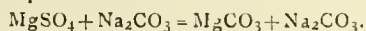
Lime will thus only remove temporary hardness.

When caustic soda is used the reactions are:—

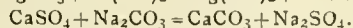
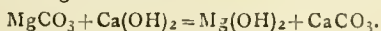


In this case the water is left alkaline with carbonate of soda, which is objectionable except where permanent hardness is present, when the carbonate will then react with this and bring about its removal.

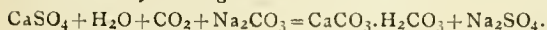
For the removal of the permanent hardness, caustic soda or sodium carbonate is required, and the latter is most generally employed. Using carbonate, the following equations represent the reactions:—



This reaction is sluggish, but if lime be employed as well the magnesium carbonate is converted into hydrate and a better softening obtained.

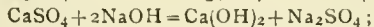
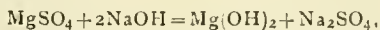


The reaction of free CO_2 or bicarbonates interferes with this process by forming soluble bicarbonate:—



Hence, in nearly all cases, lime is necessary as well as carbonate of soda for an efficient softening.

Using caustic soda, the following equations represent the reactions:—



i.e., calcium sulphate is not removed by caustic soda, but if free CO_2 or bicarbonates be present sodium carbonate will be formed, and this will remove the calcium sulphate (see equation above). Caustic soda is only suitable under exceptional circumstances when the permanent hardness is chemically equivalent to the temporary hardness. Thus, by a suitable combination of reagents, waters of varying hardness and of varying composition can be successfully softened.

Before proceeding to a description of the plants for water softening it should be pointed out that however efficient a lime or lime and soda plant may be, it cannot entirely remove all hardness from the water, this being due partly to the solubility of calcium carbonate and partly to excess of lime left in the softened water. At the very best the hardness is reduced to 2° Clark, or 3 parts per 100,000, but generally the hardness is nearer 5°.

Plants for Water Softening.

In 1841 Clark invented a process of treating water with lime to remove carbonic acid and bicarbonates of lime and magnesia. Shortly after a process of removing sulphates of lime and magnesia was invented by Porter, and a combination of these two methods is now called the Porter-Clark process. Clark's plant consisted of three settling tanks, one for mixing the hard water and lime water, a second one from which softened water is being drawn, and a third kept in reserve.

The Porter-Clark process consists in the application of machinery to the ordinary Clark's process.

The Gaillot and Huet (also known as the Stanhope) process is a continuous one, lime water and sodium carbonate being employed as reagents. The clear saturated lime water is made by passing a certain definite proportion of the incoming hard water through the milk of lime contained at the bottom of the lime saturator. The saturated lime water containing solid particles in suspension gradually rises in the saturator, the solid particles meanwhile gradually falling down and clear saturated lime water is discharged at the top. The lime water is mixed with the hard water, to which also a definite quantity of soda solution is added from a separate tank, and the mixture is led to the bottom of the clarifying tower. This contains diaphragms fixed to alternate sides. As the water rises slowly in the tower the precipitated salts settle out on the diaphragms, slide down to their lower ends, and are there removed by suitable sludge cocks. The last traces of suspended matter are removed by means of a wood-wool filter placed in the upper part of the tower.

The Lassen and Hjort apparatus is one of the most efficient plants of the present day, and differs from most softening plants in its method of adding the required

chemicals to the water. The hard water to be softened is led into the plant by a pipe which alternately fills each compartment of a two-chambered tipper oscillating on a shaft carried in bearings. When one of these compartments is full of water the disturbance of equilibrium causes the tipper to overbalance and discharge its contents of water into the tank in which it is suspended. At the same time the other compartment of the tipper is brought under the orifice of the inlet pipe, and filled in its turn with hard water to be discharged in the same manner when full. At each discharge of water from the tipper a definite quantity of reagent is discharged from the semi-circular chemical container affixed to the side of the tipper tank. This is effected by means of the positive discharge valve placed in the bottom of the chemical container, which is opened at each movement of the tipper and caused to deliver into the reaction chamber the exact quantity of softening reagent required. The chemicals are generally milk of lime and sodium carbonate. The valve can be easily adjusted to discharge any specified quantity of reagent. The mixture of hard water and reagent passes to the bottom of the reaction chamber, where the greater part of the precipitated salts settle out, and the water rising in the chamber finally passes through a wood-wool filter before passing to the storage tank.

Another type of plant is the Paterson Osilometer By-pass type, in which a certain proportion of the incoming hard water is by-passed through the "Osilometer." This is a two-chambered tipper operating somewhat similarly to that described under "Lassen and Hjort" apparatus. The main quantity of hard water drives a water-wheel, which works agitating paddles in the chemical tank. These agitators are fitted with cups which fill the reagent measuring bucket, the excess continually flowing back into the tank. The tipping of the Osilometer overturns the reagent bucket, the contents of which mix with both the water from the Osilometer and the main supply from the water-wheel. Further purification of the softened water is similar to that described before.

Other water softening plants are those of Kennicott, Boby, Royle or Reisert, Bell Bros., and Archbutt and Deeley. These are all lime or lime and soda plants, and differ only in mechanical working from those previously described. The Archbutt and Deeley plant is, however, not continuous, and differs from the others in that the softened water is finally carbonated. This is to neutralise the free alkali, and thus prevent the deposit of further sludge through the further action of the alkali on any remaining hardness.

[L. Archbutt states that the chief action of re-carbonating is the conversion of Mg(OH)_2 into MgCO_3 (*Proc. Inst. Mech. Eng.*, 1898, p. 404; *Abs. in Journ. Soc. Chem. Ind.*, 1899, p. 292)].

Plants operating with saturated lime water are becoming obsolete, because as from 10 to 25 per cent of the total supply of water has to be by-passed through the lime saturator the plants have to be very large. It is also difficult to get constant saturation on large plants. Again, many waters contain impurities which coat the lime in the saturator and render it ineffective.

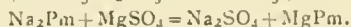
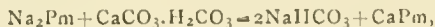
GROUP II.—Permutit Process.

This process is comparatively modern, but its use is rapidly extending on account of the simplicity of its action and the softness of the water produced. It is a process of softening water without the addition of chemicals or the formation of sludge. The hard water, either crude or partially softened, is passed through a bed of granular material called "Permutit." The process is not one of ordinary filtration; i.e., no solid matter is thrown out as a precipitate, and it is, in fact, most essential that the water be perfectly clear before entering the plant.

Permutit is a sodium aluminium silicate corresponding to the formula $3\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{Na}_2\text{O} \cdot 6\text{H}_2\text{O}$, and to-day is manufactured at Brentford by the interaction of sodium silicate and sodium aluminate. It is marketed as hard

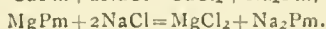
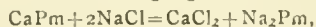
bining granules, and in appearance somewhat resembles coarse quartz.

During the passage of the hard water through a bed of this material the sodium atoms are exchanged for those of calcium and magnesium. Representing permutit as Na_2Pm , the following equations represent the reactions involved:—



Similar equations will represent the reactions for magnesium bicarbonate and calcium sulphate; *i.e.*, the bicarbonates of calcium and magnesium are converted into sodium bicarbonates, the sulphates of these metals into sodium sulphate. All traces of calcium and magnesium are removed and a water of zero hardness results. By long continued filtration of the hard water the whole of the sodium can be replaced by calcium or magnesium, or the two together, but this is not done in practice as zero water would not be obtained throughout the process. According to the hardness and the quantity of permutit employed a certain definite quantity of hard water is passed through before the process of regenerating the permutit begins. It has been found by experience that water containing much magnesium salts requires a larger proportion of permutit than one only containing salts of calcium.

The regeneration or revivification of the permutit is accomplished by a solution of common salt, which is employed in 10 per cent strength, and should be free from magnesium chloride. The following equations represent the reactions involved during regeneration:—



Sodium permutit is regenerated and the calcium and magnesium chlorides which are formed are soluble and washed away to the drain by the wash-water. It will be noticed that no sludge is formed. The method of working is as follows:—

Before introducing the salt solution the permutit is agitated by causing the water to enter the bottom of the filter. This loosens the permutit and removes any air channels which may have been formed during the softening process. After agitating for a few minutes the salt solution is allowed to flow into the permutit from the top and to percolate slowly through, the speed being arranged so that regeneration lasts about ten hours. The salt solution remaining in the filter is now washed out, and after completion the softening recommences.

In cases where the water to be softened is very hard and where it is required to have a water of zero hardness, the ideal system would be to remove the greater part of the hardness by a lime and soda plant, and the remaining hardness by the permutit system.

Although there are to-day in this country plants operating successfully by this method, there are others which have gone wrong after a period of years. The permutit has gradually become contaminated with chalk, and ultimately fails to soften the water. The cause of this is undoubtedly due in the first place to the alkalinity of the water coming from the lime and soda plant. This alkalinity, due to free lime, sodium carbonate, or caustic soda, is unavoidable, and can only be kept within limits by careful working. It affects the permutit in one or more ways.

1. Free lime passing through the permutit will produce caustic soda which will gradually dissolve it.

2. Sodium carbonate passing through the permutit already containing some calcium permutit will produce sodium permutit and calcium carbonate, the latter sometimes passing onward and giving the water an opalescent appearance.

3. Free alkali causes a further deposit of chalk to occur, this being formed from the residual hardness not completely removed in the preliminary softening. It is well known that water, even after filtration through wood-wool,

will on further filtration through sand deposit a further amount of chalk; *i.e.*, the water is further softened. The sand acts as an accelerator of the softening action; *i.e.*, it brings about the same effect as allowing the water to further stand for some hours. The permutit undoubtedly acts in the same way, only possibly in a more energetic manner, owing to its porous nature.

It is the opinion of the author that the reason of permutit failing is to a greater extent due to the action mentioned under (3) rather than (1) and (2), because in those cases where permutit works successfully after previous softening, the water has a more or less long period of rest before it enters the permutit system. This period would allow the reaction mentioned under (3) to take place before the water entered the permutit plant. The author is further led to this belief because the water in question did not enter the permutit plant for two to three days after previous softening with lime and yet was still alkaline.

A method has been tried for overcoming this difficulty of the alkaline water. Calcium permutit possesses the property of absorbing free lime, the compound supposed to be formed being represented as CaPmCaO . The calcium permutit is regenerated by passing hard water through in the reverse direction, the lime softening this water and being removed as chalk which is washed away to the drain. Although this method works well for a short period the calcium permutit loses its efficiency, and free lime again passes through without being absorbed.

Assuming that a method will be found to overcome this difficulty of alkaline water it is probable that a plant consisting of three separate systems; *i.e.*, lime and soda plant, followed by, say, calcium permutit, followed by sodium permutit, would be more expensive to work than a sodium permutit system operating directly on the crude hard water.—*Society of Dyers and Colourists*, xxxiv., No. 12.

THE CONFIGURATIONS OF ORGANIC COMPOUNDS AND THEIR RELATION TO CHEMICAL AND PHYSICAL PROPERTIES.*

By ARTHUR MICHAEL.

IN this paper the physical and chemical properties of the stereomeric, unsaturated acids will be co-ordinated with the configurations given in the first communication (1), as far as the experimental observations at hand permit, with a critical revision of previous views in this field.

Owing to the imperfect and inadequate experimental data, a perfectly satisfactory treatment of the subject is not possible at present; even in the few existing systematic investigations, not infrequently the members of the series most important from the viewpoint of theory were omitted, as beyond the scope of researches.

The Relations between the Physical Properties and the Configurations of Unsaturated Acids.

Density.—The removal of hydrogen from contiguous carbon atoms proceeds with their greater segmentation (2), which should augment the increase in gravity already produced by the elimination of the lightest known matter. This change should be in a direct relation to the number of the removed atoms, provided substances with similar configurations and in the same or a strictly comparable state of molecular aggregation are compared (3).

That such an increase takes place with unsaturation was shown by Buff (4), and was confirmed by the later work of Schiff (5), Lossen (6), Zander (7), and Weger (8), who found that the values of the increments vary considerably in different substances. A reinvestigation of the subject is necessary, however, as the conclusions of

* From the *Journal of the American Chemical Society*, xl., No. 11.

these chemists were based largely on the comparison of the compounds with dissimilar stereo-structures. That progressive unsaturation, with formation of bodies of comparable configurations, really proceeds with increase in density is shown by the data on the *l*-amyl esters, given in Walden's (9) research on their specific rotary power.

To follow the relations between the position of unsaturation in the aliphatic, monobasic acids and the density increase, it should be borne in mind that the relatively heavy carboxyl group is here the dominating factor in the specific gravity, and that therefore the density values decrease with the increasing molecular weight of the hydrocarbon radical. On the other hand, the density should rise in unsaturation with the nearness of the unsaturated hydrocarbon group to the carboxyl, as the segmentation of the axial Δ -carbons is proportional to such a relation. α,β -Unsaturation of a saturated acid augments the density decidedly more than it does in the β,γ -position, and that the difference in the effect due to β,γ , γ,δ and δ,ϵ -unsaturation is comparatively slight, is evidently in agreement with theory. The observations at hand do not permit quite sure conclusions on the connection of density with structural and stereo-structural chemical changes in unsaturated acids, but it is very probable that the replacement of a nuclear hydrogen in acrylic acid by a primary alkyl group, causes a decrease in the order of *cis*-, *trans*-, and α -substitution, and also with the molecular weight of the radical. Although the density relations in stereomeric substances are proportional to the magnitude of the compression at the axial carbons, it does not follow from this connection that the density relations and those of the heats of combustion, and in the case of acids of the affinity constants, always run parallel to each other. For the chemical nature of the axial groups may be such, that the segmentation due to the change of energy at the axial Δ -carbon atoms may not be proportional to the decrease of bound energy in the axial groups, or to that of the negative energy relations at the acidic hydrogen atoms (10).

As far as is known, however, the fumaroid form shows a greater density, excepting in the esters of maleic and fumaric acids (11) and those of allocrotonic and crotonic acids.

Since a reversion in the energy relations of maleic and fumaric acids occurs in the formation of the sodium salts (12), there is evidently a possibility of a corresponding change taking place, but to a less extent, with esterification. The catalytic transmutation of the maleic into the fumaric esters (13) shows, however, that this is not the case, although their physical and chemical properties and their energy relations are much closer together than those of the acids. The carboxyl group in esterification evidently loses much of its negative energy, and the esterified carboxyl groups in fumaric acid, that are *cis*- to the nuclear hydrogen atoms, become less capable of neutralising the positive energy of these atoms, and this results in a separation of the axial carbon atoms. On the other hand, the same change in maleic acid, by reducing the negativity of the carboxyl groups which are in *cis*-position, increases their attraction, *i.e.*, it causes an approach of the axial carbon atoms. Moreover, the *cis*-, much more than the *trans*-relation of the carbalkyloxy groups allows a better intra-molecular neutralisation of the chemical forces in them, through which the axial segmentation in the maleinoid ester is increased to a greater extent. Esterification, therefore, causes a relative reversal in the segmentation relations of the axial carbon atoms, and to an extent sufficient to give slightly larger densities to the maleic esters (14).

The substitution of a nuclear hydrogen atom in these esters by a methyl group, introduces the different influences of *cis*- $\overset{5}{\text{C}}\text{H}_3$ in a fumaric ester, and *trans*- $\overset{5}{\text{C}}\text{H}_3$ in a maleic ester to the oxygens of one of the carbalkyloxy groups. The positive influence of this methyl group is evidently greater in the fum. derivative, which explains

why the densities of the (fum.) mesaconic esters become higher, although only very slightly, than those of the (mal.) citra-compounds.

The experimental data on the densities of the ethyl esters of allocrotonic and crotonic acids are less satisfactory, but it is probable that the allo-derivative has a slightly higher value (15). In allo-crotonic acids the $\beta\text{-CH}_3$ is in the *cis*-5,6-, and in crotonic acid it is in the *trans*-5,6-position relative to the oxygens, and esterification may displace their density relations, which are probably not far apart in the acids, in favour of the mal. derivative.

J. Traube (16) has examined the molecular volume of the sodium salts of 6 pairs of stereomeric acids in dilute, aqueous solution. The salts of allocrotonic, dibromocrotonic (94°), cinnamic, furfuralacrylic, fumaric, and mesaconic acids show a larger volume than those of the stereomeric acids, and classifying the acids according to Wislicenus, Traube concluded that the salts of *trans*-acids show a larger volume than those of the *cis*-stereomers. This conclusion is not tenable, since allocrotonic is a *cis*-acid, and the dibromocrotonic acid melting at 94°, is not, as was assumed, a derivative of crotonic, but of allocrotonic acid.

Traube found further that the molecular volume of allocrotonic acid is somewhat, and that of citraconic acid considerably greater than those of the stereomeric acids, and concluded, as this is also the relation existing between the affinity constants, that the connection is explained by the difference in the "ionisation" of the acids. This conclusion cannot be considered proven on account of the meagre experimental data, and no explanation was given why an increase in the "ionisation" should cause an increase in the molecular volume.

Solubility (17).—In the solution of an acid in water a neutralisation of its negative energy to a greater or lesser amount by the positive energy of the solvent occurs, and the solubilities of stereomeric acids should stand, therefore, in a direct relation to their affinity constants, that is, the mal. form should show the greater solubility. Further, there should be an approximate proportionality between the differences in the affinity constants of such structurally related acids and those of their solubilities. The first conclusion could not have been drawn, *a priori*, and, the latter relation is not valid, in the case of some β -halogen ethylenic acids, in which a reversion of the energy relations in the mother acids took place with the substitution of hydrogen by halogen. For instance, with the conversion of (fum.) crotonic acid into the (mal.) β -chlorocrotonic acid, the less solubility of the fum. mother acid might possibly have outbalanced the effect of the change in the energy relation (18). Actually, however, in all known cases the maleinoid shows a greater solubility in water than the fumaroid form (19). The rule does not necessarily apply to other solvents, even when, like water, they are relatively basic towards acids, *e.g.*, mesaconic acid is more soluble in ether than citraconic acid. Whether a relation exists between the affinity constants and the solubility factors in such solvents cannot be determined at present, owing to inadequate experimental data. Generally speaking, however, the maleinoid stereomer in all classes of ethylenic derivatives shows in solvents a greater solubility than the fumaroid body.

Melting Point.—Carnelly (20) connected the higher value in isomeric compounds with the more symmetrical structure, to which the rule of the writer (21) for stereomers conformed, that is, the fumaroid spatially more symmetrical form shows the higher melting point. This rule still holds for the stereomeric mono α - and β derivatives of acrylic acid. With stereomeric, disubstituted β -products, it is impossible to decide which of two forms has the more symmetrical structure, and with β -halogen derivatives of stereoisomers, whose melting points differ considerably, the maleinoid modification may have, as has been explained before (18), the higher value.

This relation may also appear in derivatives of such stereoisomeric acids, where the carboxyl group has been modified chemically. Thus the chloride of the mal. β -chlorocrotonic acid is a solid (94°) and the fum. derivative is a liquid, and the melting points of the naphthyl esters conform relatively to those of the acids. If the hydroxyl groups of these acids are replaced by NH_2 , that is by a radical which in this position is decidedly positive to hydroxyl (22), the maleinoid melts lower (100°) than the fumaroid derivative (110°), and it is not impossible that the energy relations have been reversed in these compounds. On the other hand, the anilide (124°), naphthyl amide (169°), and phenylhydrazide (130°), of the mal. chloro-acid, in which NH_2 is replaced by less positive radicals, melt higher than those of the fum. derivative (105°, 155°, 114°) (23).

The former rule, that the fumaroid form always shows the higher melting point, is, therefore, too general and requires modification in the above sense. The explanation of the relation between melting point and structural or stereo-structural symmetry, should be based on the relative free energy contents of the compounds. According to the "thermo-chemical law of structure" (24) the symmetry of positive radicals in isomeric substances towards a common negative nucleus is connected with an increase in the heat of formation, i.e., with diminution of free energy, and this is also true in stereoisomeric bodies. As the change in the state of aggregation consists in overcoming the intermolecular attraction to a certain degree, it seems in accordance with the less free energy in the more symmetrical isomer and stereomer, that a greater heat increment is necessary to bring them into the liquid state (25).

Boiling Point.—Boiling may be considered a continuation of the melting process; and the same reason why the fumaroid should melt higher than the maleinoid form exists in regard to their boiling-point relations. The former rule (26) that the fumaroid stereomer shows the higher boiling-point is still valid, with the exceptions that occur in the relations between the esters of several dibasic ethylenic acids, where the maleinoid products show somewhat higher values (27). When one of the acidic hydrogen atoms in maleic acid is replaced by sodium, the free positive energy still residing in the metal is further converted into bound energy and heat by the oxygens of the remaining carboxyl group. This final conversion is possible only to a much lesser degree in the corresponding acid fumarate, owing to the greater distance in space between the metal and the respective oxygens (28). Corresponding changes occur again in the formation of the neutral salts, and the energy relations in them are close together, but the reverse of those in the acids, that is, there is an excess of positive energy in the fumarate, and probably, also, in the maleate, but certainly more free energy in the first than the latter salt. This mutation in the energy relations is plainly manifest in the gradual change in the properties of these and analogous derivatives. It shows itself, for instance, in the much greater values of the secondary affinity constants of fumaric and mesaconic than those of the maleic and citraconic acids; in the greater value of K_1 for the acid sodium fumarate than for the maleate (29); in the alteration of the titration curves for fumaric and maleic acids, which are about the same after half neutralisation but are very different before (30), and in the oxidation of potassium fumarate to the salt of the more acidic racemic acid (31), while the decomposition of fumaric acid dibromide, by boiling, gives the weaker mesotartaric acid (32).

A similar change in energy values occurs in the conversion of maleic and fumaric acids into their acid and neutral esters, since in the esterification process a neutralisation of acidic energy takes place. In the acid esters the difference in the energy contents must be much less than in the acids, and that in the neutral esters should either approximate each other, or the relations might even be reversed.

The latter contingency is barred by the catalytic convertibility of maleic and citraconic esters into fumaric and mesaconic esters, and we should therefore expect from the energy relations, that the boiling-points of these products should lie close together, but that the first-named esters should show somewhat lower values. Evidently, an unusual factor of importance enters into the property in this class of derivatives, which may possibly be that the maleinoid esters have a smaller specific heat than the fumaroid derivatives, and which could well cause the anomalous relationship in the boiling points.

For reasons explained above, the difference in the energy relation of maleic and fumaric acids and their homologues decreases with the replacement of nuclear or acidic hydrogen by primary alkyl groups (33), and as it should, in a direct proportion to the size of the radical. The boiling-points of such derivatives are in agreement with theory; thus, the difference, which between the methyl esters of the maleic and fumaric esters is 15°, falls to 7° in the ethyl esters; and that between the methyl esters of citraconic and mesaconic acids is only 5°, which decreases in the ethyl esters to 2.3° (34).

Viscosity.—According to Reyher (35) the viscosity constants of the sodium salts of aliphatic acids increase, generally speaking, with the decrease of the affinity constants of the corresponding acids; later Lauenstein (36) showed that irregularities occur, which are particularly noticeable in the salts of the aromatic acids. As sodium is a strongly positive metal, there is an excess of positive energy in such salts of most monobasic organic acids, and the viscosity relationship appears to stand in a direct relation to the free, positive energy in the salt.

In accordance with such a relation, the viscosities decrease with unsaturation; thus, in passing from (*cis*) sodium succinate to the comparable sodium maleate, the viscosity falls from 1.3914 to 1.2399, to increase with sodium fumarate to 1.3371. Although, in the next homologous series the values of the salts of the unsaturated acids are less than that of the saturated derivative, and in accord with the K_1 relations are larger than those of the maleate and the fumarate, the relations in the salts of the two saturated acids and in those of the ethylenic acids in the series are displaced (37). Viscosity is a developed constitutive property, and the relation existing between it and the energy content would doubtless appear more marked, if compounds existing in solution in a strictly comparable molecular condition were used as the basis of comparison.

Notes.

1. *Journ. Am. Chem. Soc.*, 1918, xl, 704.
2. *Journ. Am. Chem. Soc.*, 1918, xl, 706.
3. Unless otherwise stated, this molecular relation is assumed in the paper.
4. *Ann. Suppl.*, IV., 1865, 158. In this remarkable paper the relation between the molecular volume of inorganic and organic compounds and state of saturation was first formulated.
5. *Ber.*, 1882, xv., 1270; *Ann.*, 1883, ccxx, 291.
6. *Ann.*, 1882, ccxiv., 121.
7. *Ibid.*, 1882, ccxiv., 138.
8. *Ibid.*, 1883, ccxxii., 102.
9. *Zcit. Phys. Chem.*, 1896, xx., 583.
10. See footnote under heading "Heat of Combustion" (prox.).
11. Anschuetz, *Ber.*, 1879, xii., 2280; Perkin, *Journ. Chem. Soc.*, 1890, lviii., 585; Walden, *Zeit. Phys. Chem.*, 1896, xx., 383 and 583; Walden and Swinne, *Ibid.*, 1912, lxxix., 738.
12. Michael, *Am. Chem. Journ.*, 1908, xxxix., 14.
13. Anschuetz, *Ber.*, 1879, xi., 2282.
14. The densities of the acids do not differ very much i.e., that of fumaric acid is 1.625 and of maleic acid is 1.590 (Tanatar and Tchelebijs, *Journ. Russ. Chem. Soc.*, 1890, xxii., 549). The value for ethyl fumarate is 1.0496

and for the maleate is 1.0658, both at 25°. With the increase in the size of the alkyls, in the replacement of nuclear and also of acidic hydrogen, the difference in the gravities decrease, which is in agreement with theory.

15. The value for the crotonic ester is 0.924 at 20° and for the allocrotonic ester it is 0.927 at 19° (Geuther, *Zeit. Chem.*, 1871, xiv., 243). The latter value should be somewhat larger, as the allo-acid used contained more than 50 per cent of crotonic acid.

16. *Ann.*, 1896, ccxc., 69.

17. Michael, *Journ. Prakt. Chem.*, 1895 [2], lii., 345.

18. *Journ. Am. Chem. Soc.*, 1918, xl., 710.

19. The two α -methyl- β -chlorocrotonic acids (Otto and Holst, *Journ. Prakt. Chem.*, 1890 [2], xli., 475; *Ber.*, 1894, xxviii., 948, 1351), if they are stereomeric, stand in the same relation to tiglic and angelic acids as the β -chlorocrotonic do to crotonic and allocrotonic acids. That is, the higher melting acid (73°) is a derivative of the fumaroid tiglic acid, but is maleinoid, because the halogen in it is *cis*- to the carboxyl group and it is, therefore, more soluble in water.

20. *Phil. Mag.*, 1882 [5], xlii., 116.

21. *Journ. Prakt. Chem.*, 1894 [2], lii., 345.

22. Michael, *Ibid.*, 1899 [2], lx., 430; 1903, lxviii., 496.

23. Autenrieth, *Ber.*, 1896, xxix., 1665; Autenrieth and Spiess, *Ibid.*, 1901, xxxiv., 189.

24. Michael, *Journ. Am. Chem. Soc.*, 1910, xxxii., 1004.

25. Werner ("Lehrb. d. Stereochemie," 211) appears to have overlooked the work of Carnelly, Franchini (*Rec. Trav. Chim.*, 1897, xvi., 142), and the writer, and whatever original information he has added to the subject is not tenable. His suggestion that para and fumaroid derivatives have similar configurations is unwarranted, as stereo-structural relations in such aromatic compounds are not known, and the assumption would imply the existence of stereomeric para derivatives. It is, also, arbitrary to assume symmetry in the structure of para in contrast to that of ortho compounds, as is evident by placing the groups in the first class of substances on the apexes of the hexagon, and not, as Werner has done, on the opposite sides. The connection between the melting points of aromatic isomers and structure is the same as that of fatty isomeric and stereomeric substances; that is, generally speaking, the body with smaller energy content shows the higher figure. Some of the exceptions to the rule may be explained as has been shown in the first paper, e.g., the reversed order in *p*-chloro-*o*-toluic and *o*-chloro-*p*-toluic acids which stand in the fum. and mal. relation, analogously to the reasons given for that in β -chloroallocrotonic and β -chlorocrotonic acids (*Journ. Am. Chem. Soc.*, 1918, xl., 710).

26. Michael, *Journ. Prakt. Chem.*, 1895 [2], lii., 345.

27. Anschütz, *Ber.*, 1879, xi., 1644; 1880, xii., 2280.

28. Michael, *Am. Chem. Journ.*, 1910, xxxix., 14; Michael and Cobb, *Ann.*, 1908, cccxliii., 68, where the similar influence of ortho-hydroxyl group is discussed.

29. Ostwald, *Zeit. Phys. Chem.*, 1892, ix., 559; Chandler, *Journ. Am. Chem. Soc.*, 1908, xxx., 694.

30. Thiel and Römer, *Zeit. Phys. Chem.*, 1908, lxxiii., 725.

31. Kulé and Anschütz, *Ber.*, 1880, xlii., 2150; xiv., 713; Michael, *Am. Chem. Journ.*, 1908, xxxix., 14.

32. Lossen and Riebensalm, *Ann.*, 1897, ccxcii., 295; 1899, ccc., 5.

33. The relation doubtless prevails, too, with secondary and tertiary radicals; the differences in this particular, and in some other physical properties, should decrease in the order of primary, secondary, and tertiary group.

34. Evidently, the difference between the energy contents of ethyl citraconate and mesaconate is inconsiderable; in esters with so positive a radical as the tertiary butyl (Michael, *Journ. Prakt. Chem.*, 1899 [60], lx., 423, footnote 4 and 432), the relations may be slightly reversed. That such changes in the energy relations are induced not only by aqueous solution, and by partial neutralisa-

tion of the acids in question, but also by esterification, is ample evidence of the insufficiency and untenability of the explanation based on the ionisation hypothesis (Ostwald, *Zeit. Phys. Chem.*, 1892, ix., 558).

35. *Zeit. Phys. Chem.*, 1888, ii., 744.

36. *Ibid.*, 1892, ix., 417.

37. This subject will be considered in a later paper. (See *Journ. Am. Chem. Soc.*, 1918, xl., 119, footnote 2).

(To be continued).

CONTROL OF METALS, CHEMICALS, MACHINERY, AND PLANT.

PRIORITY FOR ORDERS INVOLVING THE USE OF METALS.

FOR the guidance of manufacturers it is desirable to recapitulate the modifications in the control of material and machinery which have been made to date by the Ministry of Munitions since the cessation of hostilities.

I. Priority.

(a) Ordinary civil orders may now be placed and executed in Class C without priority permits or certificates. No further applications need, therefore, be made to the Priority Department of the Ministry of Munitions unless it is desired for national reasons to raise the priority of an Order.

(b) Uncomplete contracts for the Admiralty, War Office, and Ministry of Munitions, which have been placed in Classes A or B, need no longer be given the priority attaching to them under the Order of Priority of March 8, 1917, except in cases where the contractor is notified in writing or by official notice in the Press that a particular classification is still required to be given to any particular contract.

II. Metals.

(a) *Modification of Control.*—(1) Iron, Steel, and Non-Ferrous metals may be ordered, supplied, and used for Class C Orders without priority classification or reference number from the Ministry of Munitions; and stocks purchased and held by Government Contractors may be used for any class of work. (2) No permit is now required for the manufacture or sale of Iron and Steel Wire or Wire Rope for Home Trade, and until further notice manufacturers of Forgings, Stampings, and Castings in Iron, Steel, or Malleable Iron are at liberty to accept orders for priority below Class B. (3) The Control Orders forbidding dealings in Non-Ferrous Metals without a licence are suspended in the case of Tin, Copper, Brass (including swarf and scrap), Cupro-Nickel, Scrap, Spelter, Lead, Platinum, Chrome ore, and Type Metals. (4) All restrictions as to the sale or purchase of Calcium Carbide have been removed subject to a maximum price to consumers of £40 per ton for quantities of 1 cwt. and over.

(b) *Export Licences.*—(1) Manufacturers must still continue as hitherto to obtain licences for export for articles made of Steel and Non-Ferrous Metals covered by the various schedules of the War Trade Department, but every effort will be made to grant these licences as freely as possible.

(c) *Prices.*—(1) The maximum prices of steel for Home Trade are to continue at their present level until February 1, 1919, when the direct subsidies paid by the Government on Steel will cease, and a corresponding increase in price take place. A schedule of the prices to come into force on February 1 can be obtained on application to the Ministry of Munitions (C.I.S.P., Room 104, 8, Northumberland Avenue, S. W. 1). The present maximum prices of Pig Iron are to remain unchanged until April 30, 1919, but post war conditions are not yet sufficiently stable to warrant a fixing of prices after that date. (2) A schedule of fixed Report Prices for Pig Iron and Steel, to take effect from November 18, 1918, has been issued, and can be obtained on application to the Ministry of Munitions,

as above. The prices which are based upon the existing home prices, *plus* the subsidies paid by the Government, will remain in force until further notice. Upon all exports of Pig Iron, onmanufactured Steel, and certain classes of semi-manufactured Steel, a drawback will be collected by the Board of Customs and Excise, equivalent to the amount of the subsidy already paid by the Government on the articles in question. The items on which the drawback is chargeable are those whose prices are controlled and included in the schedules referred in the preceding paragraph. Application for the schedule showing the amount of the drawback to be collected should be made to the Board of Customs and Excise, Lower Thames Street, London, E.C. (3) The following is a schedule of the present prices of Non Ferrous Metals from holdings of the Ministry:—

	Buyers, per ton.	
Copper, electrolytic	£125	Delivered works.
Brass ingot to Government specification	£93	Do.
Spelter—G.O.B.	£57	Do.
Refined 99.9 p.c.	£61	Do.
Aluminium	£200	Do.
Solt pig lead	£40	Ex-steamer or ex-store.

(The existing schedule in relation to manufacture in lead is abolished).

Nickel	£195	Ex-works or warehouse.
Antimony	£55	Do.

(These prices are subject to usual extras for small parcels).

III. Chemicals, &c.

(a) *Alcohol*.—Alcohol and Methylated spirit are now available for industrial purposes, and can be obtained through the usual channels subject to the regulations of the Board of Customs and Excise.

(b) *Glycerine*.—Arrangements have been made to enable Glycerine Producers to supply their customers with substantial supplies of glycerine for general use.

(c) *Shellac*.—The Shellac Control Order of March 12, 1918, prohibiting dealing in shellac except under licence, has been revoked.

(d) *Benzol, Naphtha, Chlorine, &c.*—The Orders prohibiting dealing, &c., in Benzol, Naphtha, Tar (Coal and Water Gas), Chlorine, and Chloride Compounds, and Acetic Acid are suspended.

(d) *Building Bricks*.—The present controlled maximum prices for bricks are not to be reduced, provided the present system of control continues, for a period of six months from January 1, 1919.

IV. Plant and Machinery.

1. Restrictions as to dealing in and prices of new and second-hand machinery and treadle lathes have been withdrawn; but purchases of new machinery can only be made from firms holding trade permits from the Ministry of Munitions.

2. Contractors in possession of plant and machinery owned by the Ministry of Munitions are at liberty to use it for civil work provided they notify the Superintendent Engineer in their area within one week from the date on which it was first used. If the Contractor does not ultimately wish to purchase the machinery he will be required to pay a reasonable hire not to exceed the rate of 20 per cent per annum on the cost price of the machine.

3. The Crane Order of December 30, 1916, prohibiting the sale or supply of any Cranes except under permit, and the Motor Engines and Vehicles Order of January 6, 1917, prohibiting the manufacture except under permit, are revoked.

4. The Orders of March 30, 1917, prohibiting the experimental manufacture of Aeroplanes, and of May 10,

1918, prohibiting the experimental manufacture of Aero-Engines, are suspended.

5. Owners of Steam-driven Lorries and Trailers are no longer required to make returns of changes of ownership.

FINANCE FOR TRADE.

THE Committee on the provision of Financial Facilities for Trade after the War was appointed jointly by the Chancellor of the Exchequer and the Minister of Reconstruction in November, 1917, under the Chairmanship of Sir Richard B. Vassar-Smith, of Lloyds Bank. They introduced their Report (now published by the Ministry of Reconstruction) by expressing the emphatic opinion that the primary factor in repairing the wastage of capital caused by the War lies mainly in increased production and actual saving.

Discussing the financial requirements of industry after the War the Committee foresee:—

- A considerably more than normal demand for working capital owing to the higher cost of labour and materials, the necessity for giving longer credit, and the anticipated expansion in the volume of trade due to the fact that the basis for potential commercial output, as compared with pre-war output, has been very greatly enlarged during the war by the extension of existing works and the building of a very large number of absolutely new ones.
- A greater than normal demand for extended credits for the purpose of replacing at higher cost machinery and plant which has fallen into disrepair.
- Demands in connection with the reconversion of plant and works. These in many cases may be on the border line between working credit facilities and new capital requirements.
- New fixed capital requirements for extensions or new works.

The Committee point out that the ability of industry to cope with these unusual financial problems during the reconstruction period will be most limited in the case of entirely new firms which have come into existence owing to the demand for war material. They have been urged strongly that it was not in the national interest to allow these firms to peter out, and that every inducement should be given them to continue in business, even to the extent, if necessary, of granting State financial assistance. The Committee express the opinion that it might be regarded as unjust to enable such firms by means of State aid to compete with old-established firms in the same industries, and also that it would be very difficult, if not impossible, to guard against wastefulness and inefficient management. The solution in these cases appears to them to lie in the establishment of new industries, the capital for which should be furnished by the investor or by the individual partners in the business. The ability to attract the necessary capital will depend upon the inherent soundness of the proposition in each case.

The Committee further point out that it would be of great assistance to manufacturers in making plans for the future if the future policy of the Government were made known as early as possible in regard to—(a) Fiscal policy; (b) Rationing of raw materials; (c) The break clause in connection with the termination of Munition Contracts; (d) The disposal of National Factories and surplus stores.

Before discussing means of providing credit facilities after the War the Committee give a short explanation of our Credit System as existing before the War.

In normal times the amount of credit varies with the amount of gold, the necessity for keeping the gold standard effective acting as an automatic check upon the expansion of credit. As the balance of indebtedness of this Country with Foreign Countries became unfavourable, and the exchanges in consequence moved against us, it

became profitable to export gold to pay debts abroad. The constant shrinkage in the amount of gold in the Country, and the reduction in the Bank of England ratio of reserve to liabilities, necessitated a rise in the Bank rate, which in its turn brought about a general rise in rates of interest. This rise in interest rates had a two-fold effect. It attracted gold to this country, and induced gold, which would otherwise have been exported, to remain; secondly, it induced people to pay off loans and discouraged the raising of new ones. If the drain of gold was severe enough to make money "tight," it became difficult to renew existing loans, and this caused the sale of goods and produce upon which the loans were secured, so bringing about a fall in prices, which encouraged exports and discouraged imports, so that the situation was gradually adjusted.

Further, from the point of view of purely internal trade, the fact that gold was the only legal tender was equally effective in preventing an undue expansion in credit. Banks being obliged to maintain a proper relation between the extension of credit facilities and their available supply of gold. Thus the gold standard acted as a wholesome restraint upon overtrading, and often adjusted situations, which unchecked might have developed into a severe commercial crisis.

The position to-day is entirely different. As there is no free international market in gold, the operation of the foreign exchanges has been interrupted, while at the same time the internal gold circulation has been replaced by a currency note issue. As there is no legal limit to the amount of currency notes which may be issued, there is therefore no automatic check upon the expansion of credit. The very large extent to which expansion has taken place is shown by the fact that whereas the total deposits at the banks of the United Kingdom, exclusive of the Bank of England, amounted at the end of the year 1913 to £1,070,000,000, the amount of deposits is now nearly £2,000,000,000. The enormously increasing purchasing power thus created has, in the Committee's opinion, been one of the main factors contributing to the general rise in prices.

In regard to the position after the war the Committee express the opinion that it is essential for the reconstitution of industry and commerce to impose restrictions as soon as possible upon the creation of additional credit by the restoration of an effective gold standard. To attempt to rebuild industry by the further indiscriminate expansion of credit would endanger our position as the financial centre of the world, and would inevitably lead before long to grave disaster. The Committee accordingly seconded the cessation of State borrowing as early as possible, all available money being required for the financing of commerce and industry. The Committee also consider that any Government guarantee to bankers to enable them to provide by means of credit for fixed capital expenditure for the reconstruction of industry is undesirable, as being likely to occasion a further expansion of credit followed by an additional rise in prices. It is also recommended with a view to the gradual reduction of credit inflation, arising from the enormous volume of short dated Government debt, that the State should undertake funding operations at an early date for this purpose.

As to banking facilities for carrying on ordinary businesses the evidence submitted to the Committee led them to the opinion that the situation might safely be left in the hands of the banks. To enable the banks to give facilities for extended credit it is recommended that every facility should be given by the Government to enable the banks to issue any new share capital which may be found necessary to strengthen their position. It is thought that the rationing of available supplies of raw materials will provide a valuable guide to the banks in selecting the directions in which loans will be best secured and are most urgently required.

The policy of trade organisation which is now in

evidence is welcomed by the Committee as furnishing a sound basis for the granting of credit facilities to industry. They also believe that if a portion of the new issues of shares, which will be necessary for many manufacturing establishments, in the form of preference shares giving a good return in dividends, were reserved for the workpeople in these establishments, it would materially assist both financially and in other equally important directions.

The Committee consider that the continuance of some measure of State control over new issues is desirable for a certain period, and that with a view to the further prevention of unsound promotions the Companies Acts might be strengthened. The enormous potential increase in the number of small investors, as shown by the figures published by the National War Savings Committee, and the importance of the encouragement of this tendency for the rapid reconversion of trade and industry, are emphasised by the Committee, as is also the necessity for genuine saving to make good the destruction of capital during the War.

In regard to State aid, while the Committee does not recommend the guaranteeing of banks by the Government or the investment of public money in loans to persons who have been unable to obtain them from other quarters, it is considered that cases of hardship may arise in connection with firms who have undertaken, under considerable pressure from the Government, the manufacture of munitions of war. To meet such cases the Committee suggest the establishment of a small Committee of Government officials and business men in leading industries to consider claims of this kind in the first instance, or to act as a tribunal to which applicants can make appeal. The Committee are also of opinion that it would be of very great assistance to manufacturers and others, who had been prevented from forming adequate reserves by the present high rate of Excess Profits Duty, if arrangements could be made by which a proportion of the tax should be retained for a period as a loan upon terms likely to secure early repayment.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 21, 1918.

Prof. W. J. POPE, C.B.E., F.R.S., President,
in the Chair.

THE PRESIDENT referred to the loss sustained by Society, through death, of the following Fellows:—Richard Pendarves Hodges, Edgar Dingle Jones, John Sydney Keel.

Messrs. S. J. Green and A. L. Bloomfield were formally admitted Fellows of the Chemical Society.

Certificates were read for the first time in favour of Reginald Christopher Bickmore, 5, Clarence Road, Sydenham Road, Croydon; Stanley Edward Bowrey, B.Sc., 115, Hainault Road, Leytonstone, E. 11; Benjamin Richard Heasman, B.Sc., Rutherglen, Throwley Road, Sutton; Harry Jephcott, M.Sc., 43, King Henry's Road, Hampstead, N.W. 3; John Parrish, B.Sc. Tech., Ringwood, The Green, Sidcup, Kent; Ernest Edward Pendlebury, "Moss Bank," 184, Wellington Road, Eccles; Francis Henry Sweeting Warneford, B.A., B.Sc., 21, Rochester Avenue, Sedgley Park, Prestwich, Manchester; Leo Daft Williams, 16, Hauteville Court, Stamford Brook, W. 6; Charles Thomas Woosnam, M.A., 22, Royal Avenue, Lowestoft.

The meeting was then adjourned and the Informal Meeting declared open.

NOTICES OF BOOKS.

Coal and its Scientific Uses. By WILLIAM A. BONE, D.Sc., Ph.D., F.R.S. London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. 1918. Pp. xv+491. Price 21s. net.

THE author of this book, as Chairman of the British Association Fuel Economy Committee in 1915-17, had many opportunities of acquiring information relating to various aspects of the coal question of the present day, and is thus particularly well qualified to present an authoritative account of the subject from the scientific and technical points of view. Apart from this special qualification he possesses a marked gift for clear exposition and succinct summarising of the essentials of a subject, and he is to be heartily congratulated upon having produced a work of great and permanent scientific value, which gives British industrial users of coal a means of obtaining the most recent and reliable information upon the statistics, chemistry, and technology of coal. The first part of the book contains a chapter upon the importance of the coal question to the welfare of the nation and empire. The author's statements as to coal reserves, and their probable duration, the output per worker, &c., demand very careful and serious consideration, and in some respects are by no means reassuring. The chapters on the chemical composition of coal give an admirable survey of modern work, which the author has summarised in a masterly manner, bringing together trustworthy information from all sources and explaining with great lucidity the underlying principles. The sections on the carbonisation industries are thoroughly practical, as well as the chapters on domestic heating and on fuel economy in steel works, where the author is perhaps at his best. As a contribution to the literature of industrial chemistry it may confidently be predicted that the book will long be regarded as a model of comprehensiveness and judicious selection from a vast store of material. The author exhibits great skill in arranging his facts and summarising them, and users of coal owe him a debt of gratitude for this admirable work.

Colour in Relation to Chemical Constitution. By E. R. WATSON, M.A. (Cantab.), D.Sc. (Lond.). London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. 1918. Pp. xii+197. Price 12s. 6d. net.

A VAST amount of research work on the causes of colour, and its dependence upon chemical constitution has been done in this country, and up to the present time no complete review of all the results obtained, here and abroad, has been prepared. Hence this volume should be specially acceptable to chemists who are engaged in the dyeing industries, and who require a general *résumé* of facts and theories. The research worker in the region will find it of the greatest possible value, showing him clearly the exact state of our knowledge, and pointing out in what directions work is wanted and what lines of investigation may very possibly lead to fruitful results. While the author has not attempted to review every research which has been undertaken he has succeeded in summarising the chief results which have been obtained in such a way as to enable his readers to follow the development of our knowledge of the causes of colour as far as it has gone, and the most important theories which have been put forward are admirably discussed and criticised. In the first chapter early observations and theories are described, and the value of the rules of Witt and Armstrong and Nietzki as working guides is fully recognised. The quinonoid theory and its modifications are then adequately discussed, and general methods of studying absorption spectra are treated fully. Many plates showing the absorption curves of typical colouring matters are reproduced, after a short account has been given of graphical method of repre-

senting results. In the later parts of the book modern theories are well discussed, and a short account is given of the study of the infra-red absorption spectra of organic substances. In dealing with the colour and spectra of inorganic substances the author warns his readers against accepting the view that the colour of inorganic and organic substances is due to different causes, and he gives a short general summary of the colours and absorption spectra of the elements under ordinary conditions, and of the absorption spectra of simple compounds in gaseous form.

Chemical Combination among Metals. By Dr. MICHELE GIUA and Dr. CLARA GIUA-LOLLINI. Translated by GILBERT WOODING ROBINSON. London: J. and A. Churchill. 1918. Pp. xiv+337. Price 21s. net.

THE great value of the method of thermal analysis is now fully recognised, and the literature dealing with its application to metallic systems has become so extensive that a summary of it in English will certainly be acceptable to metallographists. The monograph opens with a general account of equilibrium diagrams and a discussion of the nature of intermetallic compounds, the work of continental investigators being perhaps given somewhat undue prominence. The accurate study of the physical properties of intermetallic compounds—conductivity, specific heat, hardness, &c.—is then taken up, and finally all the known compounds are described individually and in detail. The facts included have been brought together from many sources, and the value of a compilation of them for English readers is at once obvious. The diagrams of each compound are clearly printed, and the same scheme has been adopted in the preparation of all of them. A short chapter is added on the work which has been done on ternary compounds.

Report of the Committee of the Privy Council for Scientific and Industrial Research for the Year 1917-18. London: H.M. Stationery Office. Price 4d. net.

THE year ending July 31, 1918, saw a great extension of the work of the Committee which is chronicled in this Report. A National Fuel Research Station has been erected at East Greenwich, and the Council has undertaken the responsibility of the maintenance and development of the National Physical Laboratory. The Laboratory has been extended in order that it may undertake the testing of the higher grades of chemical glass and the testing of all clinical thermometers. The establishment of a Food Investigation Board has been sanctioned, and a series of special committees has been appointed to deal with particular aspects of the subject. A Research Board has also been established to continue and develop the researches into the production of tin and tungsten in Cornwall, and various important investigations have been sanctioned, such as a series of tests of home grown timber which, it is hoped, will afford useful guidance in the re-forestation of the country. Satisfactory progress has been made with the negotiations between the Department and the industries of the country for the establishment of industrial research associations. The scheme described in the last Report has been found satisfactory in all essential points and has required modification in detail only. Grants have been made to various undertakings, such as the British Scientific Instrument Research Association, the British Photographic Research Association, while conditional promises of grants have been made to the British Cotton Industry Research Association and to the future British Research Association for the Woollen and Worsted Industry. The Report of the Advisory Council is divided into two parts. The first describes the progress which has been made in the establishment of research associations and the steps that have been taken in the organisation of national research. Departmental publications are also enumerated, the work of the Standing Committee

is referred to, and some account is given of the organization of research in the Dominions beyond the seas. Some thirty industries are already actively engaged in preliminary work for the establishment of Research Associations, and Board of Trade Licences have already been issued to three of these—the British Photographic Research Association, the British Scientific Instrument Research Association, and the British Wool Research Association.

At the National Physical Laboratory researches on optical glass have been carried out, and investigations of heat transmission through hot surfaces, and the quality of oiliness in lubrication oils are in course of progress. The Board of Trade is arranging for the transfer of their Electrical Standards Laboratory to the National Physical Laboratory. The Director of the Fuel Research Board has during the year continued to give advice to the Admiralty and Ministry of Munitions in connection with urgent war problems, and has set on foot an enquiry into supplies of oil for naval, military, and industrial purposes. He has also been supervising the experimental work necessary to obtain data upon which to base advice to the Board of Trade on the technical question of gas standards. A representative has been appointed to make inquiries in the United States on the use of coal-dust firing for steam boilers and furnaces, and grants have been made to the Meteorological Office for work on atmospheric pollution and to the Institution of Mining Engineers for their investigations into atmospheric conditions in deep and hot mines.

A Central Board has been appointed with various Sub Committees to inquire into the preservation of food by coal storage, and experiments upon the freezing of fish are being conducted at North Shields. The Meat Committee has begun work upon processes of putrefaction, the chemistry of post-mortem change in flesh, and the preservation of beef by cold. The Ministry of Food has also called upon the Board to assist them in connection with the use of oils and fats. The appointment of a responsible Director to organise a group of researches of national importance assisted by an advisory board of men of science and affairs has been fully justified by events, and it may be regarded as certain that research work, like other forms of creative activity, will not flourish under committee rule.

A Tin and Tungsten Research Board has been appointed to consider the possibilities of successful mining in Cornwall, and reports embodying the results of their researches have been published from time to time. The first steps have been taken to set on foot investigations of artificial processes for drying timber, and improved methods of sterilising against timber diseases, and specimens of all timbers felled for war purposes have been collected and indexed. A research upon the suitability of building materials and the construction of cottages has been begun, a special Committee having been appointed to direct it. The Department has been consulted as to the desirability of initiating a comprehensive investigation of industrial fatigue, and the relation between the hours of work and output, and has come to the conclusion that the best means of approaching these problems is to establish a small central Research Board, to be assisted by a panel of representative men and women from each of the industries to be studied, who will join the Board as each trade in turn comes under review. Such a Board has been appointed, its object being:—"To consider and investigate the relations of the hours of labour and of other conditions of employment, including methods of work, to the production of industrial fatigue, having regard both to industrial efficiency and to the preservation of health among the workers."

In Part II. of the Report some account is given of the more important developments which have taken place in the conduct of researches. The investigation of the atmospheric corrosion of metals has been extended, and a report upon the production of a marketable hard porcelain

manufactured from British materials has been presented. The problem appears to have been satisfactorily solved, and it was decided to permit the recipes for the new body and glaze to be communicated freely to firms who could satisfy the Research Committee that they were likely to make bona fide use of the discovery. A preliminary report has also been received upon a research into the acoustics of the pianoforte. The new aided researches include the investigation of insulating materials, and of information as to the phenomena of arcing and switching.

The policy of making personal grants to students and research workers has been carefully reviewed, and the Council is of the opinion that it is not advisable to embody their views in detailed regulations for the award of research fellowships and studentships, but to consider each application individually and personally. They have not yet considered it advisable to recommend any grants to inventors.

The Report closes with a short discussion of the question of the supply and salaries of trained scientific workers. The proposed remedies for the deficiency of science students are summarised, but it is pointed out that far-reaching educational reforms will have to be undertaken in order to cope with the emergency—"the problem is part of the wider problem of increasing the number of university trained students in general, and cannot be solved by measures conceived in the special interests of science, or by reforms which affect one part of the educational system while leaving the other parts untouched.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxvii., No. 13, September 23, 1918.

This number contains no chemical matter.

No. 14, September 30, 1918.

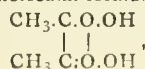
Heterogeneity of Steel.—H. Le Chatelier and B. Bogitch.—When polished steel is attacked by various reagents such as dilute sulphuric acid, tincture of iodine, and cupric solution, the results are visible to the naked eye, and the authors have made a study of this macrographic method of revealing the heterogeneity of steel. The quality of steel is directly related to this macrographic heterogeneity, which appears to be due to the presence of oxygen in solid solution. It has long been known that oxygen is present in the fused metal, undoubtedly as FeO, and at the moment of solidification it is supposed to become separated from the metal. However, some of it appears to remain in solid solution, not uniformly distributed, for the parts of the steel which solidify last would be richest in oxygen.

No. 15, October 7, 1918. No. 16, October 14, 1918.

These numbers contain no chemical matter.

MISCELLANEOUS.

The Constitution of Acetic Acid.—The vapour of acetic acid at 135° C. has a density of 3.01, at 300° C. it is 2.08. The most natural assumption, one that is borne out by facts, is that at the lower temperature 50 per cent of the vapour has a molecular formula—



the density at 300° corresponding to CH_3COOH . The specific heat of acetic acid vapour taken as 0.4 would indicate an absorption per grm.-molecule of $0.4 \times 165 \times 60$; i.e., 3960 cal. through the range of temperature in which this change takes place, and corroborates conclusions (CHEMICAL NEWS, Jan., 1906) drawn for a carbon atom changing from a single to a double linking as in the simpler formula $\text{H}_3\text{C} \begin{smallmatrix} \text{O} \\ \parallel \\ \text{OH} \end{smallmatrix}$. These conclusions, drawn from a comparison of heats of formation, justify the above formula, as does the specific heat. The double formula lending itself to a possibility of stereo-isomerism there may be quoted a divergence in the determinations of the boiling-point, the slight alkalinity of the normal sodium salt, whilst the calcium salt is neutral, and hence slight differences in titrating with caustic soda or lime-water. Also acetic acid of the maximum density takes place with a union of 67.7 parts of acid and 18 of water; with a hydrate, $\text{C}_2\text{H}_4\text{O}_2 \cdot \text{H}_2\text{O}$, it would be in the ratio 60:18, and isomers might dissociate variably. Acetic anhydride has a density almost identical with the maximum for acetic acid, hence the possible persistence of the double structure of acetic anhydride, $\text{CH}_3\text{--CO} \begin{smallmatrix} \text{CH}_3\text{--CO} \\ \parallel \\ \text{O} \end{smallmatrix}$, in the molecule of acetic acid.—J. C. THOMLINSON, B.Sc.

Faraday Society.—A General Discussion on "The Theory of Ionisation" will be held on Tuesday, January 21, 1919, from 5 to 6.30 p.m. and from 8 to 10 p.m., in the Rooms of the Chemical Society, Burlington House, London, W. 1.

Sir J. J. Thomson, P.R.S., will preside over the Discussion.

Prof. G. Senter, D.Sc., will open the Discussion.

Prof. S. Arrhenius (Stockholm), will contribute a paper on "The Evidence for Electrolytic Dissociation."

Prof. S. F. Acree (Syracuse, U.S.A.), will contribute a paper on "Some Investigations bearing on the Present Position of the Theory of Ionisation."

Capt. J. W. McBain, Ph.D. (Bristol), will read a paper on "Some Fundamental Problems of the Dissociation Theory in Aqueous and Non-aqueous Solutions."

Mr. W. R. Bousfield, M.A., K.C., F.R.S., will read the following papers:—"On Correction of the Transport Numbers for Combined Water"; "On the Determination of the Ionisation of Aqueous Solutions."

Dr. N. R. Dhar (Paris) will read a paper entitled "Some Aspects of the Electrolytic Dissociation Theory."

Dr. Henry J. S. Sand (Sir John Cass Technical Institute) will read a paper on "The Hydration of Ions."

Prof. Albert W. Porter, D.Sc., F.R.S., will read a paper on "The Variation of Electric Conductivity of Solutions with Concentration."

Dr. E. B. R. Prideaux (Nottingham) will read a paper on "Pyridine and Ammonia—Estimation and Separation."

Capt. J. R. Partington, R.E., D.Sc., will read a paper on "The Dilution Law."

Dr. H. M. Dawson (Leeds), Prof. A. Lapworth, F.R.S. (Manchester), Dr. S. R. Milner (Sheffield), Prof. J. C. Philip, O.B.E., Prof. James Walker, F.R.S. (Edinburgh), will contribute to the Discussion.

The subject will afterwards be open for general discussion.

Determination of Coco-butter in Butter.—Chr. Barthel and Klas Soudea.—The authors have made a careful study of the following processes for determining coco-butter in butter—the refractometer method, the determination of the Polenske index (in conjunction with the Reichert-Meissl index), and the determination of the melting point of the acetate of phytosterine by Bömer's method. They find that the determination by means of the refractometer can be carried out very rapidly and easily, and is useful for determining relative quantities. It is not wise, however, to place too much reliance upon

it, although it may be regarded as a preliminary method for enabling samples to be classified as those which are certainly not adulterated and those which may be suspected. A series of determinations carried out at 40° gave for 19 summer specimens numbers varying from 42.9 to 45.1, with a mean of 43.8; for 16 winter specimens 41.5 to 44.2, with a mean of 42.8. Nineteen specimens of pure coco-butter gave results lying between 33.5 and 35.6. When samples of genuine butter to which had been added 5, 10, and 15 per cent of coco-butter were tested it was found that no conclusions as to their purity could be drawn from determinations of their indices of refraction. From 20 per cent of coco-butter the index begins to show deviations, but no definite limit can be stated below which the butter may be classed as adulterated. Pure butters may give indices between 40 and 41, and mixtures of pure butter and coco-butter may give numbers between 43 and 44. It may, however, be said that in general an index below 42 renders a further examination necessary, while an index between 42 and 44 does not exclude the possibility of adulteration. Oleomargarine gives indices between 48 and 49 at 40°, and the addition of it to a specimen of pure butter raises the index. The authors found for the Polenske index numbers between 1.7 and 3.4, while the Reichert-Meissl index lay between 25.7 and 31.2. Generally speaking, Polenske's method reveals in a specimen an addition of 5 per cent of coco-butter, but when the cows have been fed upon coconut cake or beetroot leaves the Polenske index is abnormally raised, and thus serious errors may arise. Bömer's method for determining a vegetable in presence of an animal fat is less convenient than that of Polenske, but the results are reliable. The authors have determined the melting-points of cholesterol acetate, crystallised four times, with 25 samples of pure butter, and the results lay between 113° and 115.9°. With specimens containing 5 per cent of vegetable fat half of them gave melting-points below 116°; with 10 per cent all the melting-points were above 116°, while in two cases out of six it exceeded 117°, and above that limit the specimen might definitely be stated to be adulterated.—*Moniteur Scientifique*, 1918, 924, p. 268.

NOTES AND QUERIES.

Composition of Match Heads.—The heads of ordinary matches, which will strike anywhere, usually contain phosphorus sulphide mixed with some oxidising agent, such as potassium chlorate, red lead, &c. The heads of safety matches may be made of—Potassium chlorate, 32 per cent; potassium dichromate, 12 per cent; red lead, 32 per cent; antimony sulphide, 24 per cent. The rubbing surface consists of a mixture of almost equal parts of red phosphorus and antimony sulphide.

Calcium Carbide.—The following are some books dealing with the manufacture of calcium carbide:—"Calcium Carbide and Acetylene," by F. H. Leeds and W. A. Butterfield; "L'Acétylène et ses Applications," by F. Dommer; "Acetylene," by V. B. Lewes. A German periodical, *Carbid und Acetylen*, published by J. H. Vogel, Berlin, is devoted to the manufacture of carbide and acetylene, and a complete list of articles and papers on the subject is given in Ludwig's "Fahrer durch die Gesamte Calcium-carbid und Acetylen-Literatur," Berlin.

Phosphate of Soda.—Sodium phosphate is used in medicine for making *Sodii phosphus effervescentis* and *Sodii hypophosphis*. Tribasic sodium phosphate is used largely for water softening and for preventing the formation of incrustations in boilers.

MEETINGS FOR THE WEEK.

TUESDAY, 14th.—Royal Institution, 3. "Lessons of the War," by Prof. Spenser Wilkinson.

WEDNESDAY, 15th.—Royal Society of Arts, 4.30. "English Carpets," by A. F. Kendrick.

— Society of Glass Technology, 3.15. (In the School of Technology, Manchester). "Costing Systems in Glass Works," by J. Mills.

THURSDAY, 16th.—Royal Institution, 3. "Chemical Studies of Oriental Porcelain," by Prof. J. Norman Collie.

— Royal Society of Arts, 4.30. "Coal and Mineral Traffic on the Indian Railways," by H. Kelway-Bamber, M.V.O.

FRIDAY, 17th.—Royal Institution, 5.30. "Liquid Air and the War," by Prof. Sir James Dewar.

SATURDAY, 18th.—Royal Institution, 3. "The Irish Literary Renaissance," by Rev. Canon J. O. Hannay.

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SCIENCE AND THE FUTURE.*

By ALAN A. CAMPBELL SWINTON,
F.R.S., M.Inst.C.E., M.I.E.E., M.I.Mech.E.

YOUR Council having done me the honour of electing me for a second term of office as their Chairman, it is my duty once more to deliver to you an Address on the occasion of the opening of this new session. Last year, in speaking to you of Science and its Functions, I endeavoured, by means of a rapid sketch of its origins and its progress in the past, and by some considerations of its scope and effects in the present, to show how important science is, and how largely mankind is dependent upon it for our modern civilisation.

This year I propose to advance a step farther, and perhaps with more daring than prudence, to consider some aspects of Science and the Future, together with what we may possibly expect, just in one or two directions, in the days that are still to come.

A matter which we now see constantly referred to, in every newspaper and by many public speakers, is what is known as reconstruction—that is to say, the putting of our affairs in order after the finish of the war. Now, undoubtedly the war has been responsible for an enormous amount of destruction of capital; but when estimates are given, as they constantly are given, of the percentage of loss in Belgium, France, Italy, Serbia, and other countries, it is not usually borne in mind that Capital does not merely consist of gold and silver, of bricks and mortar, of furniture and fittings, or even of railways, steamships, and machinery—mostly things that in process of time fall into decay—that the main Capital of the modern world does not consist of the concrete constructions of labour or of material things at all, out of scientific knowledge. If we could imagine such a catastrophe as destruction, on the scale that has recently taken place in the fighting zones, spread over the whole civilised world, so that nothing was left anywhere at all of the material handiwork of the past few hundreds of years, this would not necessarily mean the relapse of mankind in general to the savage state of our prehistoric ancestors, who lived before the accumulation of our present priceless scientific knowledge had even begun. That this is so we see clearly from the lessons of the past. For thousands of years the manual labourer has been at work, and untold have been the products of his toil. How many of these products, however, have come down to the present day? Where are now the splendid constructions, the magnificent buildings, the costly and varied manufactures, of ancient Babylon, Egypt, Greece, and Rome? A few scattered fragments, of a purely antiquarian interest, but of no utilitarian value, are all that are left. The greater portion have entirely disappeared. But not so the products of the ancient mind. These to a large extent still endure. For all of our industries, all our arts and crafts, and all our sciences have their roots in the distant past. Some knowledge of importance may, in the crash of empires and the great social convulsions that have taken place, have been lost or forgotten, but comparatively not much; while, owing to the invention of printing, and the consequent easy manipulation of records, this is never likely to happen again, at any rate on any considerable scale. Thus to reconstruct the material things now temporarily

destroyed will take only a very small fraction of the labour that had to be expended, or of the centuries of time that had to pass, while, by slow degrees and arduous effort, man learnt how to bring all these things about. For the mere construction of the material paraphernalia of civilisation is in value as nothing to the knowledge of how to construct them. Taking this into consideration, we recognise the fallacy of the socialist's doctrine that all wealth is due to manual labour, and we see how little of the capital of the world is really due to mere handiwork, however skilled, and how much to the mental efforts of exceptional men, who through countless generations, by their investigations, discoveries, and inventions, have rendered possible all our wonderful possessions. When, therefore, we compile estimates of the losses due to the war let us not forget that our greatest asset, the vast store of knowledge that science has gathered together, for us the heirs of all the ages, is still intact. It is a store that has slowly been accumulating ever since the beginning of the world, a store which enables man more and more to triumph over Nature, and one that forever remains practically indestructible as the real permanent capital of the race, and by far its most precious heritage.

Now, though the devastation due to the war will in time be readily enough repaired, and this without any call for new scientific invention or discovery, it is otherwise with the general future. Though the doctrine of Malthus—that whilst the population increases in geometrical ratio, the supply of food only increases in arithmetical ratio—is now discredited, the war in fact has shown us how nearly the world lives up to its supply of food and other necessities, and how disturbances, such as those that the war has occasioned, may lead to the disappearance of the little margin that there is. Were it not for the aid that Science already affords to agriculture—in mechanical means of cultivation, and in methods of irrigation, fertilisation, and the like, together with facilities as regards transport and countless other matters—neither a country like this, nor the whole earth, could even now support their present populations; whilst in the future, as human beings increase still further, the stress will be accentuated. It is stated in no less reliable a handbook than *Whitaker's Almanack*, that "it has been estimated that the earth can maintain a population of 6,000,000,000 souls—a total which will be reached about A.D. 2100 at the present rate of increase." I have been unable to obtain the foundation for this statement, but if it is correct the urgency of the matter is obvious, more pressing indeed than the question of the exhaustion of our coal that is so often mentioned, and with regard to which I shall have something to say later on. For if once the stage were reached where the population increased more rapidly than the means of its sustenance, than either by famine or by reduction in the reproductivity of the race, addition to the population would have to be checked, and it is difficult to believe that either Leagues of Nations or anything else would have the power to prevent conflicts between peoples struggling in dire necessity for the vital means of existence. Such conflicts have no doubt taken place locally in the past history of our globe, and it is for Science to prevent or to delay as long as possible, if it cannot eventually preclude, the world-wide repetition of such disasters. Anyway, whether we are dealing with present-time requirements or with those that are more remote, the shortage of the necessities of life and of civilisation that is bound to grow in extent, *vis à-vis* of the increase of the population of the world, can only be met by new achievements in the way of scientific discovery and invention, and by improved and more scientific organisation.

As time goes on all industries must tend to become more intricate and elaborate, and more and more dependent for success, on the one hand upon the skilful management of the specially trained, and on the other upon the general mass of the workers intelligently and cheerfully submitting to the technical direction of minds

* An Address delivered at the opening meeting of the 165th Session of the Royal Society of Arts on November 20, 1918. From the *Journal of the Royal Society of Arts*.

more gifted than their own. This applies to the educated workers as well as to those who are uneducated.

Luckily the need for scientific brains is at last becoming recognised by every class, even by the Labour Party, and we are not now likely to see, at any rate in any civilised country, a recurrence of the attitude of the revolutionists of 1794, who sent the great Lavoisier to the scaffold with the gibe that the Republic had no need for chemists.

Thus in the future, if the industries of this country are to flourish in the face of the world's competition, it is above all things necessary that Science should play a greater part in them than it has in the past. In most departments of industry the old rules of thumb are obsolete, and if they have not already been superseded the sooner that they go the better. The modern world has no room for antiquated and unscientific methods. But in arriving at the conditions that are desirable, manufacturers will require all the help they can get, and especially they should be able to look for assistance from the Government of the country. Much in this direction is, it is satisfactory to know, already under way. The National Physical Laboratory, which, under the direction of Sir Richard Glazebrook, to whom our Society has this year awarded its Albert Medal, is doing a great work in assisting technical industry. Until recently it has been carried on at the risk of the Royal Society, but is now to be guaranteed its requisite finance from Treasury sources. Similarly the Advisory Council has been furnished by the State with funds with which, in combination with manufacturers, Research Associations are being instituted for the purpose of carrying out scientific investigations useful to the needs of different descriptions of manufacturing trades. All this is in the right direction and will, it is to be hoped, be increased so as to operate on a still larger scale. Whatever sums, however large, the Government can be induced to spend in thus promoting the applications of Science to industry, provided the expenditure is wisely directed, will quickly repay themselves many times over by the increase of prosperity that they are certain to bring about. At the same time let us beware of Government control, which in the long run is sure to result in political interference, and consequent disaster. All experience goes to prove this, and not least the experience that has been gained during the past four years of war. Here, no doubt, under the spell of patriotic enthusiasm, and owing largely to the self sacrifice of hundreds of our best brains, almost incredible things have been accomplished in the huge munition factories that have been organised by the State. The cost, however, has been prodigious, as also the waste, and while such procedure is justified in order to meet the exigencies of war, in times of peace such arrangements could never prove economic, or stand for a moment the test of competition from other industrial countries. Whatever may be possible under war conditions, in ordinary times the incentive of personal gain cannot be dispensed with, while it is idle to compare production, on the scale and under the conditions that have recently obtained in munition factories, with what can be looked for under ordinary trade conditions, where the expenses of finding and keeping markets—expenses that do not exist in the case of Government war contracts—have to be met. Moreover, while opinion is unanimous in advocating the advantages to be gained by the State doing all it can to stimulate and encourage the application of Science to industry, it is only necessary to consult the manufacturers of the country, who have had experience during the last few years of Government control, to obtain equally convincing evidence of the petrifying and sterilising effect of the latter, and how it hampers and, indeed, tends to kill enterprise at every turn. Time does not avail here to analyse the reasons, but even the most experienced and capable of business men seem to become paralysed both as regards initiative and as regards getting things done, when once caught in the tentacles of the bureaucratic machine. Hence when one sees advocated in the Press, as has recently been the case, that certain key industries

should be safeguarded by being placed under Government control, one can only hope that no such mischievous advice will ever be followed. By all means let there be Government assistance, but the less Government control the better.

Now to turn to a different subject. "If instead of a little smattering of Latin, which the children of the common people are sometimes taught . . . and which can scarce ever be of any use to them, they were instructed in the elementary parts of geometry and mechanics, the literary education of this rank of people would perhaps be as complete as it can be." Thus wrote Adam Smith in his "Wealth of Nations," and he proceeds to recommend the "instituting some sort of probation even in the higher and more difficult sciences to be undergone by every person before he was permitted to exercise any liberal profession, and before he could be received as a candidate for any honourable office of trust or profit."

This was written nearly a century and a half ago, and the controversy of Science versus the Classics is still with us. It is a final phase of the old controversy in connection with authority, chiefly the authority of Aristotle, but also of the Church, which did so much to impede the progress of Science throughout the Middle Ages. It is largely bound up with the matter of the subjects set in examinations, and dependent upon the vested interests of teachers and examiners, who, having themselves been brought up upon the Classics and knowing little or nothing of Science, are naturally disposed, in self defence, if for no other reason, to inculcate the shoemaker's maxim that there is nothing like leather. Signs are, however, now not wanting that at length the claims of Science in education are beginning to be recognised. The lessons of the war and the visions of industrial competition, keener than ever, that are already presenting themselves, are having their effect. Just as at the present day it is difficult for us to understand how the dictates of classical authority some hundreds of years ago put a bar to scientific investigation, so in the future it will be considered almost incredible that up to the second decade of the twentieth century the learning of dead languages and the study of their dry bones was considered a better preparation for an active career than the pursuit of living science, with all its practical application and its insight into the wonderful world in which we live. In putting forward, however, the advantages for all and sundry of a scientific education, far be it from me to decry the study of classical literature as a relaxation, or even as a serious occupation, for the minds that are naturally drawn that way. By all means let us have a few great Classicists, just as have a few real poets, though we can do without the smaller fry in both spheres. But for the ordinary person who wishes to refresh himself with the heroic epics of Homer or of Virgil, the subtleties of Plato, or the graceful fancies and the delicate diction of the Greek Anthology, let him do here what he already does, certainly with no loss, in the case of Holy Writ, and read the translations that have been made by the great masters, which are assuredly much better than any he is ever likely to produce for himself. Nor, indeed, must I be supposed to depreciate the teaching of history or of foreign languages, and especially of our own—all matters of great importance even to the man who proposes to devote himself to a purely scientific career. For what I presume is intended to be the object of general modern education is first of all to impart such a knowledge to the average boy as will fit him to be a good citizen, and secondly to give everyone, in whatsoever station of life he may be born, the opportunity of development; in the early stages to the best extent of which he is capable, with proper chances and encouragements for the future later on, should he give promise of exceptional ability in any direction. The history of Science in the past is largely made up of the lives of men who were self-taught, but the groundwork of most sciences is daily becoming more intricate and abstruse, and consequently more difficult to acquire. What is necessary is

the teaching of this groundwork, and then opportunity for expansion. We know, as I have said, of many instances of great scientists who were self-taught, but we know nothing of the others who might have been their equals had they ever, by a little rudimentary teaching, been started on the scientific road. As has been well said, "The literature of Science might have been quite different if Faraday had missed the unique opportunity afforded him by Davy at the Royal Institution. How many Faradays have remained mute and inglorious because doors were closed?"

There is one method of acquiring a scientific education to which, in my opinion, not nearly enough attention is paid. I refer to the private reading of technical books and of periodic scientific literature. In the past many of our leading scientific men have owed their education almost entirely to this method. Faraday was a book-binder's apprentice, and obtained his first introduction to Science by reading the books that were sent to his employer to be bound. The first Lord Armstrong, who was the inventor of the hydraulic method of transmitting and utilising power, and was also the father of modern gunnery, had no advantage in the way of scientific teaching, and, as he himself once told me, acquired his early knowledge of Science almost entirely by reading. Other distinguished scientists and inventors who educated themselves in this way were the Scotchman, Alexander Graham Bell, who has received the Albert Medal of this Society for his invention of the telephone, and Thomas Alva Edison, the renowned American inventor, who also has received the Albert Medal for the invention of the phonograph, and who, when a lad, was so voraciously a reader that he is said to have started to read the "Encyclopædia Britannica" right through from end to end, though history does not relate how far he got with this ambitious project. There have also been many others who never had the advantage of any scientific teaching either at school or college, and yet achieved great distinction. No doubt these were exceptional men, but how many more such might there not be if greater facilities existed. It is not within the power of many young men to buy books to any great extent, and scientific literature is not only expensive but is notoriously ephemeral, becoming rapidly obsolete and comparatively valueless. Most of the large scientific libraries such as are possessed by the various engineering institutions and other scientific societies are only accessible to their members, who have to pay heavy subscriptions, and even then only during hours which to a large extent preclude their use by those who have to earn their livelihood, and have therefore little time but the evenings available for reading. Such libraries, moreover, only exist in London and in a few of the large towns. No doubt the war scarcity of persons suitable as attendants is in part responsible, and makes any change at the present time very difficult, but I am convinced that whenever possible these libraries should be kept open on Saturday afternoons and in the evenings. Indeed, if necessary it would be much more useful to keep them open till, say, ten o'clock at night even if this necessitated their not opening at all till after mid-day. I put this forward from the actual experience of students, members of some of our leading engineering institutions, who complain that their libraries are useless to them as they are only open at hours when they are perforce otherwise engaged. I am sure that some improvement is possible, at any rate after the war, in this respect; but what I am anxious particularly to put forward is the desirability of the establishment of lending libraries from which all the latest scientific works could be obtained under suitable arrangements. The Institution of Electrical Engineers has of recent years instituted such a lending scientific library, but only to its own members and on a comparatively small scale; but, of course, to be of any wide use such an arrangement must be on a large scale and throughout the country. It is suggested that something more in this direction might be done by the Patent

Office, who have large funds available entirely derived from the fees paid to them by inventors. No doubt the Patent Office already provides a splendid library in London to which the public are freely admitted, but this might be supplemented by additional similar libraries, in all our large towns, with facilities for lending the books out by means of a special free postal service, on a system embracing the whole country. Anyway, what is wanted is to encourage self-education in scientific and technical subjects, so that those who have not the time or the opportunity to attend classes and lectures, or even to frequent libraries, where reading can only take place *in situ*, can improve their knowledge by reading at home in their spare time. It is impossible also to exaggerate the utility of public or semi public lectures on scientific and technical subjects in spreading knowledge in these subjects and stimulating curiosity, thought, and also invention. Throughout its long existence the activity of the Royal Society of Arts in this direction is well known, and must have had a profound and wide-spread effect, not only on those who have been able to enjoy the advantage of attending the lectures, many of them by the highest authorities in their various spheres, but also of reading accounts of them in the *Journal*. In our case the object and the achievement have mainly been of a technical nature, applied rather than pure science being what this Society has chiefly in view. In pure science the lectures at the Royal Institution have undoubtedly been a stimulus to thousands, and the same may be said of the lectures in all the philosophical and scientific societies throughout the country. The ultra erudite are sometimes rather inclined to sneer at such lectures as popular and superficial, but it is exactly by such popular lectures that general interest in Science can be roused, rather than by the dryer and more strictly scientific dissertations that we expect at professional, scholastic, and university institutions.

(To be continued).

WATER SOFTENING.

By E. V. CHAMBERS.

THE textile industries in the North of England owe their success in a large measure to the ample supplies of upland surface water. Such water has a very low degree of hardness, contains but little suspended solids, and up to the present has been freely available in unlimited quantities. The probability is that this water would be even more suitable for textile requirements were it not for the fact that a portion of the water is used for domestic purposes. Untreated upland surface water has been found to exert a chemical action on the lead service pipes supplying domestic dwellings, so that lead poisoning has been prevalent from time to time. To avert this difficulty it has been the practice to treat the water with limestone and other substances with a view to neutralising the acids which attack the lead pipe, and, as a consequence, the water as delivered to a textile manufactory is somewhat harder than before treatment. Notwithstanding this, however, it may be considered a very suitable and satisfactory water.

There are two objections to the general use of upland surface supplies:—(1) Comparatively high cost; (2) growing shortage of supplies.

Speaking with regard to its cost, it will be conceded that if an equally suitable water can be obtained at something less than half the cost of Corporation water, the latter becomes dear by comparison, and there is no question that a softened water can be obtained at much less cost than that taken from the public supply.

As to the growing shortage of upland surface supplies, Dr. Wilson, of the West Riding of Yorkshire Rivers Board, at a meeting in Huddersfield of the Textile Insti-

ute, drew attention to the fact that the shortage of upland surface water would shortly become a very serious matter for the industries of the West Riding. He stated that owing to the many new industries now being established in the Riding, with a consequential increase in the population, very careful consideration of the water supplies available was essential. He made many useful suggestions and also outlined a constructive policy of water conservation, more particularly in the nature of the purification of waters which had been once used in textile and other processes. His statements should be carefully considered by anyone engaged in the textile and allied industries.

It often happens that for one reason or another Corporation water must be substituted by another supply, and from another source. Difficulties may then arise, such as those described by Mr. King in the previous paper, and so far as our knowledge and experience go, the only way out of the difficulties referred to is in the direction of the installation of a water softener.

It then becomes a question as to the selection of a water softening plant, and whether such a plant can eradicate the difficulties brought about by the use of a more or less impure water.

Water softening is a chemical operation, and therefore factors of proportion, time, and temperature apply as in other chemical reactions. These facts cannot be too well known. Out of a varied practical experience one learns at least as much about the difficulties of water softening as one does of its advantages. Many of these difficulties can be avoided by selecting the right type of plant for the work required of it, and when the water to be treated exceeds a moderate hardness the lime and soda type of apparatus is a necessity. This type of plant when properly designed and with due attention will give satisfactory results. It will produce a water which will satisfactorily replace the Corporation supply in most cases, while the actual cost of the soft water may be only one-fifth of that of Corporation supply. There are two general types of lime-soda water softening plants—the intermittent and the continuous types. The intermittent type possesses several advantages. This plant usually consists of two large tanks, each tank holding at least four hours' supply of water. The process works intermittently, so that when one tank of water is being softened the other tank is being filled with hard water. The volume of water in the tank is known, and to this measured volume of water of known hardness a weighed quantity of lime and soda is added—the lime in the form of milk of lime and the soda in solution form. The contents of the tank are then thoroughly mixed and allowed to settle. After a certain time the calcium and magnesium compounds are precipitated, settling to the bottom of the tank, when the clear softened water may be drawn off for direct use, or into a store tank. The precipitated solids are drawn off by an outlet in the bottom of the tank.

Owing to the great facilities for control this is probably the most exact method of water softening, and with an ordinary hard water practically the whole of the hardness-forming salts can be removed, and the softened water contains the minimum excess of lime and soda. In a works where there is sufficient room for the tanks, and when the first cost of the plant is not of importance, it is doubtful whether any process can give more satisfactory results.

The continuous process of water softening has for certain reasons received more attention than the intermittent process. This is mainly due to the fact that the plant occupies less room and requires less attention than in the intermittent system.

By the latter process, working on a four hours' cycle, a plant to deal with 5000 gallons of water per hour would require a total capacity of 40,000 gallons. On the other hand, a continuous plant of the same capacity would not require a tank capacity greater than 15,000 gallons.

To work successfully a continuous plant must meet the following conditions:—

1. The lime and soda control system must work accurately.

2. The tank capacity must be large enough to enable the chemical reaction to complete itself fully.

3. The lime and magnesia sludge must be easily removed from the plant.

There exist many types of continuous plant, a good example of which is now to be described. This plant was designed to deal with 5000 gallons of water per hour. The capacity of the tank is 15,000 gallons, and its dimensions 34 ft. high by 10 ft. diameter.

Lime and soda sufficient for one day's charge are placed respectively into the reagent mixing tank and the lime slaking tank. After being mixed with water the lime and soda solutions are elevated by steam ejectors to the top of the plant. The soda enters the reagent reserve tank and is fed from there by a ball valve into the reagent feed tank, where it is kept at a constant level. The milk of lime gravitates by the central pipe into the bottom of the lime saturator. The hard water is pumped into the hard-water receiving tank and flows through two slot pipes, one to the lime saturator and one to the main treatment tank; the slot pipe controlling the feed of the lime saturator is adjustable and is set to displace the exact amount of lime required for the treatment which is fed into the main treatment tank, at one constant strength, being in the form of a saturated solution of lime. Should the flow of hard water vary, its level will rise or fall in the hard water receiving tank, thus passing more or less water through the slot to the lime saturator. At the same time the float in the hard water receiving tank will rise or fall, actuating the lever and dipping another slot pipe more or less into the soda. The soda slot pipe is also adjustable, and is set to feed the exact quantity of soda required to treat the hard water. The lime and soda thus apportioned are thoroughly mixed with the hard water in the central tube of the main clearing tank, down which the mixture gravitates. The treated water then enters the main clearing tank, where ample time is allowed for the chemical reaction to complete itself. The cleared water passes slowly upwards through the wood fibre filter when the water is ready for use. The precipitated hardness-forming salts are drawn off by the sludge valve at the bottom of the tank, which has a conical bottom with an angle of 60° to facilitate the removal of all the sludge. The spent lime in the saturator is also drawn off in a similar manner once a day.

It will be seen by the foregoing description that the only moving parts on the whole of the plant are the lever which is actuated by the float, and the ball valve which controls the soda level in the reagent feed tank. There is therefore little to wear out or get out of order. The reagent feed apparatus works accurately and produces a soft water of very uniform nature.

This apparatus described can reduce a water having a total hardness of 26° down to 2.5° without imparting to the softened water any appreciable excess of alkalinity. The softened water is just a little lower than that of the Corporation supply of the district. The total cost of the softened water, after making all due allowances, does not exceed 2½d. per 1000, the lime and soda being based on pre-war prices.

The statement frequently made—that a softened water may be used for any purpose—requires some qualification. Such a water is at times apt to contain an excess of softening materials, either in the form of sodium carbonate or sodium hydrate. Below a certain point this excess may be disregarded in the operations of scouring, washing, or steam raising.

In the process of dyeing, however, even a slight excess of alkalinity may cause serious trouble and particularly so when the alkalinity varies for any reason. In wool dyeing many of the dyestuffs require an acid bath; with a neutral water the exact quantity of acid can be deter-

mined, and even though the water contains considerable hardness no serious difficulty is experienced. When the water contains a varying quantity of alkaline salts it becomes practically impossible to determine the quantity of acid necessary, and the result may be that the dye is not taken up by the wool or that several dyeings of the same kind vary considerably in depth. Great care and consideration should be given to this matter before deciding to use softened water for dyeing purpose. In cotton dyeing similar difficulties may be experienced when dealing with basic dyes.

Another difficulty sometimes experienced when using a softened water is that of the deposition of suspended precipitate in the works service pipes, in store tanks, and about the steam nozzle of the injector for boiler feed. This defect is usually due to the main clearing tank of the water softener being of too small a capacity for its output of softened water, when, as a consequence, the chemical reaction is not completed in the water softener, and calcium or magnesium salts are gradually precipitated in the pipe system through the works. This defect is sometimes the cause of the heavy incrustation which forms in economiser pipes, where owing to increased temperature the chemical reaction is accelerated. The only remedy is to increase the water softening tank capacity or alternatively to reduce the quantity of water to be softened.

The working of a water softening plant should be checked daily, and a daily record kept of the results obtained. Any man of average intelligence, with the assistance of a simple set of chemical apparatus, can carry out the tests. The daily record should show—

1. Temporary and permanent hardness of raw water;
2. Hardness of softened water;
3. Alkalinity of softened water as sodium carbonate or sodium hydrate.

With these results it becomes possible to understand intelligently the results of the softening operation, and, when necessary, to vary the chemical treatment.

Any type of water softening apparatus must be adjusted to a variation in hardness of the raw water. Even in those types of plant where the water passes through a bed of softening material the time-capacity of the softening medium is reduced in ratio as the hardness of the raw water increases.

The question of the conservation of water supplies will become very important in the near future. There is certainly much good water wasted in the textile and allied industries. It is well known that in piece scouring and in washing-off after dyeing a large quantity of water is wasted. This water is only slightly contaminated with impurities, and a very simple chemical treatment is sufficient to render the water suitable for almost any purpose in a textile factory.

A water purification plant may be installed for dealing with the wash water from piece scouring. This consists mainly of two large precipitation and filtration tanks, and an automatic reagent feed apparatus, with the necessary reagent preparing tanks at ground level. The wash water from the scouring machines is allowed to pass through a special screen for the removal of fibre. It is then pumped from a large receiving tank into the softening tanks shown. It enters a hard-water receiving tank, and by an automatic system receives the necessary chemical treatment. First a little sulphuric acid is added, sufficient to decompose the soap and to liberate the grease therefrom. This grease is caught on special filters and sold to grease manufacturers. Then the water receives a fresh treatment with sodium carbonate, and after it has passed through the second tank it goes into a large reserve tank for supply to the works. The softened water has a total hardness of 4.5 grains per gallon, is perfectly clear and colourless, and is used for boiler feed purposes. It is also quite satisfactory for piece scouring and washing. The total cost of the chemicals for purifying this water works out

at 2d. per 1000 gallons on a pre-war scale. A point of interest in connection with this installation is that the works trade effluent is considerably reduced, and in such cases the effluent charges payable to the Corporation can be proportionately reduced. This type of apparatus fully justifies the statement that in future it is more than probable that large quantities of water will be dealt with by a similar arrangement, thus greatly helping to reduce the demand on original water supplies.

A water softening plant will deal satisfactorily with water drawn from the various rivers in the textile districts. River water give an average hardness of 8 to 10 grains per gallon. It usually contains oil and suspended solids. The chemical precipitation of the lime and magnesia salts simultaneously carries down with it the oil and suspended solids. In the worst cases the use of a little crude sulphate of alumina along with the lime and soda will produce a bright colourless water. When the hardness of the water varies a larger tank capacity will to a great extent equalise the hardness of the softened water.

Another source of water which relieves to a great extent the demand on the Corporation supply is that obtained from boreholes. This water is quite easily dealt with by a water softener. As a rule the hardness is not excessive, and therefore the cost of treatment is low.

In conclusion, it is not out of place to emphasise the fact that water used for boiler feed purposes should be treated in a water softening plant, so as to remove scale-forming substances. It is universally known that hard scale on the boiler plates and flues, and also in the economisers, considerably increases the fuel consumption. Various more or less extravagant statements have been made as to the effect of certain thicknesses of scale in the boiler. Actual boiler plant tests are more reliable, and experience has proved that it is no difficult matter to save 20 per cent of fuel as a result of removing heavy scale from the boiler. In these days this saving of fuel is a vital matter. Boiler compositions are unsatisfactory and most are absolutely useless. None of them justify their expense nor comply with the scientific requirements of the day. It is better to treat an unsatisfactory water on scientific and efficient lines. Water softening is but one of the many processes in a textile factory which will demand attention in the early future.

This country has now awakened to its potentialities. It is seen that to-day in many directions waste continues to an appalling extent. It is realised that so far as possible such waste must be discontinued.

The effluent from a moderate sized works can easily waste £1000 per annum. Soap is now being wasted to the extent of hundreds of thousands of pounds sterling per annum, owing to the use of an unsuitable water. In industry the future is to those who will efficiently apply scientific facts to technical and practical processes.—*Society of Dyers and Colourists*, xxxiv., No. 12.

Chemists—Pivotal Men.—With regard to the release of pivotal men from the Forces for employment as chemists, the Demobilisation and Resettlement Department of the Ministry of Labour has authorised the Institute of Chemistry to assist in the selection of names of chemists (professional consulting, analytical, and research) whose prompt return to civil life will prove of the most value to the country for the purposes of reconstruction and absorption of unemployed labour. The Institute is asked to select officers and men who can be classed as pivotal, preference being given to those with the longest service, and to married over single men. Works chemists are not to be included in the selection, as their employers are required to apply for them under the industry in which they are engaged. The names of selected men will be forwarded by the Registrar of the Institute to the Department of Demobilisation.

THE CONFIGURATIONS OF ORGANIC COMPOUNDS AND THEIR RELATION TO CHEMICAL AND PHYSICAL PROPERTIES.*

By ARTHUR MICHAEL.

(Continued from p. 15).

Capillarity.—Walden and Swinne (*Zeit. Phys. Chem.*, 1912, lxxix., 726) have recently determined the surface tensions and the temperature coefficients of the esters of a number of stereomeric acids. Hydrocinnamic and cinnamic esters have analogous configurations, and along with unsaturation goes an increase in the first and a decrease in the latter values. This relationship is also shown with further unsaturation, and would probably appear between the stereo-structurally analogous allo-cinnamic and phenylpropionic esters.

These chemists (*loc. cit.*, p. 746) use the capillary values of succinic and maleic *l*-amyl esters to exemplify the influence of double linkage; while the temperature coefficients likewise decrease with unsaturation, the surface tension values are practically identical. Stereomerically, the comparison is not justified as the fumaric ester is the real stereo analogue (38). The surface tension of maleic is somewhat greater than that of fumaric ethyl ester, and in the above instance, too, a decrease in the constant is undoubtedly caused by unsaturation. On the other hand, the values of chloromaleic and citraconic *l*-amyl esters are less than those of the stereomeric esters, and the interesting relationship exists that the surface tensions and the densities of these compounds stand in direct relation. This connection probably occurs in all other groups of derivatives formed in progressive unsaturation, provided they exist in like conditions of molecular association, and the two first members of the series have similar stereo-structures. For example, it is shown by the *l*-amyl esters of hydrocinnamic, cinnamic, and phenylpropionic acids.

Optical Activity.—In his researches with derivatives of *l*-amyl alcohol Walden (*Zeit. Phys. Chem.*, 1896, xx., 569) showed that ethylenic α,β -unsaturation in esters causes an increase in the molecular rotation and in the dispersion, but that the values fall in the corresponding acetylenic derivatives, although they are still larger than those of the saturated bodies.

Walden (*loc. cit.*, p. 580) concluded from these relations that the transition from double to triple linkage is accompanied by a change in the nature of the unsaturation, and Werner ("Lehrb. d. Stereochemie," 1904, p. 135) thinks that it indicates the magnitude of saturation to be greater in acetylenic than in the related ethylenic bodies.

As Walden (*Zeit. Phys. Chem.*, 1894, xv., 651) found that the fum. esters in the dibasic ethylenic series have larger values than the stereomers, the same line of reasoning led to the conclusion that the extent of their unsaturation exceeds that in the mal. esters. Obviously, this conclusion is opposed to the other physical and to the chemical properties shown in these groups of substances. These apparent contradictions are due to the comparison of substances with dissimilar configurations. Hydrocinnamic and cinnamic, or succinic and fumaric, esters are stereomerically alike; the effect of further unsaturation should not be deduced from differences between the unlike cinnamic and phenylpropionic esters, or fumaric and acetylenic dicarboxylic esters, but between those of the acetylenic derivatives and the similarly constructed allo-cinnamic and maleic esters, whose values are undoubtedly considerably smaller (39). Further, there is no way of ascertaining directly the effect of acetylenic unsaturation on the relations of these properties, as stereo structurally similar, saturated bodies are not known.

Magnetic Rotation.—In no other physical property does the effect of ethylenic unsaturation vary to such a marked extent with the chemical nature of the compounds, and

Sir W. H. Perkin (*Journ. Chem. Soc.*, 1884, xlv., 561; 1886, xlix., 205; 1888, lvi., 597; 1895, lxxvii., 261) found that it always causes an increase in the values, and also, although from an examination of only a limited number of stereomeric bodies, that a fumaroid shows a higher value than the maleinoid form.

To determine the effect of unsaturation in the stereomeric ethyl esters Perkin subtracted the values of the crotonate, oleate, maleate, and citraconate from those of the butyrate, stearate, succinate, and pyrotartrate, and found the rotations of the unsaturated derivatives to be 1.1–1.2 units greater, which he considered the normal value for ethylenic, α,β -unsaturation. Since the difference between the values of crotonic and butyric esters is about the same as that between the dibasic esters, it has been concluded that the configuration of crotonic acid "is like that of maleic acid, which is confirmed by the chemical relations" (Smiles, "Relations between Chem. Constitution, &c.," 1910, p. 510; Smiles-Herzog, *Ibid.*, 1914, p. 615); i.e., $(\text{H}_3\text{C})\text{IIC}=\text{CH}(\text{COOH})$ (Wislicenus, *Ann.*, 1888, cxxviii., 281). Perkin's conclusions were written before Bruni ("Feste Lösungen," p. 47; Ahren's "Sammlung," 1901) proved that crotonic and butyric, elaidic and stearic, and fumaric and succinic esters have analogous, fumaroid configurations, but the quotation given above was written years subsequently. Since the values for fumaric and maleic stereomers vary considerably it is evident that the normal value of ethylenic unsaturation can be obtained only from stereomers with similar stereo-structures, and that therefore the above conclusion attaching a *cis*-configuration to crotonic acid is quite as untenable from the rotation data as that of Wislicenus from the chemical was shown to be years ago (Michael, *Journ. Prakt. Chem.*, 1895 [2], lii., 349).

The difference between the rotations of the similar (fum.) fumaric and succinic, and mesaconic and pyrotartric, esters is 1.7–1.8, which is also that between β -ethoxy-crotonic and β -ethoxy-butyric esters; therefore the configuration of the first ester "is fumaroid" (Smiles and Smiles-Herzog, *loc. cit.*); i.e., $\text{CH}_3(\text{EO})\text{C}=\text{CH}(\text{COOE})$.

The correctness of this conclusion depends whether ethylenic unsaturation in all classes of fumaric esters is represented by the above figure, which is doubtful, as the difference between the fum. crotonic and butyric esters is 1.1. Evidently, no importance can be attached to conclusions based on such imperfect data, and under any circumstances, the configuration of the fum. β -ethoxycrotonic ester is not the above, but $(\text{CH}_3)\text{EOC}=\text{CH}(\text{COOE})$ (Michael, *Journ. Am. Chem. Soc.*, 1918, xl., 712).

Perkin (*Journ. Chem. Soc.*, 1892, lxi., 800; 1894, lxx., 815) applied magnetic rotation to the study of keto- and enol-tautomerisation, basing his calculations on the assumption that aliphatic ethylenic unsaturation is represented by the difference between the values for crotonic and butyric esters (1.1) and using additive values in the substitution of different atoms, or in the increment of radicals. These assumptions can only be approximately correct, which in compounds of different chemical nature, e.g., the mono- and di-ketones, may decidedly affect the conclusions regarding the quantitative proportions between the enol and keto forms. But the method may only serve to show with some degree of certainty whether a substance is the keto derivative or exists largely in that form, as no experimental data is known that gives the rotation difference between fum. and mal. fatty α,β,Δ esters. Further, it is not known whether in the enolisation of complicated keto derivatives, like acetylacetone, the mal. or fum. enol or a mixture of both of these is formed (10).

Heat of Combustion (Michael, *Am. Chem. Journ.*, 1908, xxxix., 1).—Lougouine (*Comptes Rendus*, 1888, cvi., 1290; *Ann. Chem. Phys.*, 1890, [6], xxiii., 186) in 1888 found that the heats of combustions of maleic and citraconic acids are greater than those of fumaric and mesaconic acids, and Stohmann (*Journ. Prakt. Chem.*, 1890 [2], xl., 202 and 357; 1891, xlii., 373; 1892, xlv., 530) con-

* From the *Journal of the American Chemical Society*, xl., No. 11.

cluded, from results on quite a number of related stereomeric acids, that this relationship may be generalised; that is, the unstable modification of such stereomers have the greater heats of combustion, and that they lose energy in passing over into the stable forms. Evidently, if the transmutation of a maleinoid into the fumaroid stereo-form is accompanied by the conversion of free into bound energy at the axial carbon atoms, and also spacially between the atoms grouped about them, the latter substances must have smaller heats of combustion, since in the change some of the atomic energy in the maleinoid derivatives is dissipated as heat.

Stohmann (*Journ. Prakt. Chem.*, 1892, xlv., 531) also stated that in stereomeric esters the unstable modifications show the larger heats of combustion, and lose energy in passing over into the stable forms. However, no experimental data to confirm the statement were published in his papers, and the only observations bearing on such stereomeric bodies are on maleic and fumaric, and ethyl-maleic and ethyl-fumaric, methyl esters. The greater heat of combustion of a maleinoid over that of a fumaroid acid is due to a less complete intramolecular atomic neutralisation, and the heat of conversion value should be larger for a pair of acids than for their esters, since the carboxyl group has lost considerable negative energy in the act of esterification. This is the relation found for the above mentioned liquid aromatic esters (41).

On the other hand, Ossipoff (*Comptes Rendus*, 1889, cix., 310; *Ann. Chim. Phys.*, 1890, [6], xxiii., 186) found the difference between maleic and fumaric methyl esters to be 6.1 Kg.-cals., while for the acids 6.2 (Stohmann), 6.5 (Roth), and 8.2 Kg.-cals. (Lougouine) are the ascertained values. Roth and Stormer call attention that the last value (8.2) is greater than that (6.8) for the esters, but there is no doubt that Lougouine's figure is too high, and that 6.2—6.5 represents the correct value, which is less than that between the esters.

This apparent exception to the conclusion stated above has a physical and chemical cause. First, fumaric methyl ester is a solid (102°), while the maleic ester is a liquid, and the real heat of conversion is 6.8 Kg.-cals. less than that of the heat of conversion of solid into liquid fumaric methyl ester. This value has not been determined, but Stohmann (*Journ. Prakt. Chem.*, 1890, xl., 349) found that it is considerable (4.9 Kg.-cals.) with much lower melting (78°) methyl succinate. Second, the cis relation of the carbomethoxyl groups in maleic ester permits a proportionately greater conversion of the free energy of the alkyl groups into bound energy and heat than the trans-relation does in the fumaric derivative (42).

It is evident that the heat of conversion of liquid maleic into liquid fumaric methyl ester must be considerably smaller than that of the corresponding acids, and that the values of the heats of combustion of the liquid esters must lie close together. That the maleic esters still represent the maleinoid forms is apparent from their convertibility into fumaric esters by catalysis, even then when both of the derivatives are liquids (Anschuetz, *Ber.*, 1879, xii., 2282).

Notes.

38. Bruni (*Atti Accad. Lincei*, 1904, [5], xiii., 1., 626). In accepting Bruni's results on the configurations of ethylenic derivatives, and disregarding those that lead to the classification of the acetylenic acids as fumaroid, it should be emphasised that only in this way is it possible to develop a consistent theoretical treatment of the physical and chemical properties of unsaturated compounds in their relation to configurations. Moreover, the acceptance of fumaroid stereo-structures for the acetylenic derivatives implies an enormous repellent force between radicals like phenyl and carboxyl, which does not exist, and leads also into a maze of contradictions between properties and configurations (see also *Am. Chem. Journ.*, 1908, xxxix., 12; *Ann.*, 1912, cccxc., 40).

39. These remarks apply also to the connections between configurations and the absorption spectra (Stewart, *Journ. Chem. Soc.*, 1907, xci., 208) where the relations appear to be similar.

40. A discussion of "magneto-optic exaltation" will be given in a later paper in connection with that of the Thiele hypothesis.

41. Roth and Stormer (*Ber.*, 1912, xli., 278). These chemists (*Ibid.*, p. 261) in stating that Stohmann proved the rule for isomeric acids, and also for maleic and fumaric acids, and that it has been accepted for stereomeric acids on inadequate experimental data, appear to have overlooked that Stohmann (*Journ. Prakt. Chem.*, 1895, [2], xlv., 531) showed its validity for the principal stereomeric acids.

42. Roth and Oestling (*Ber.*, 1912, xli., 37) show that "Stohmann's rule" is not valid for the isomeric pinonic and tanacetone keto carboxylic acids. Stohmann (*Journ. Prakt. Chem.*, 1890, [2], xl., 357) intended the rule only for simple ("stellungsisomeren") not for complicated acids of unlike structures, especially when the branched groups are unsaturated and in different positions to the carboxyl groups. It was theoretically improbable that the total free energy in such derivatives, which finds expression in the heats of combustion, should always be proportional to the free energy manifest at the acidic hydrogens. They state, however, that the rule holds for trimethylene carboxylic, crotonic, allocrotonic, and vinylacetic acids, in which the heat of combustion and affinity constants increase in the above order. The allocrotonic acid used in the Stohmann determinations contained at least 50 per cent of crotonic acid (Michael, *Ber.*, xlii., 322), and its real affinity constant must certainly be decidedly greater than that of vinylacetic acid. Roth and Oestling state further that the "stability" of these acids decrease in the order mentioned above. "Stability" as a general term is quite as indefinite as "decomposability" and "reactivity" (see Michael, *Journ. Prakt. Chem.*, 1903, [2], lxviii., 496, and conveys no precise meaning, unless it is co-ordinated in a particular physical or chemical system. No better illustration could be adduced than Roth and Oestling's contention that vinylacetic acid is less "stable" than allocrotonic acid, for the statement is as ambiguous and meaningless as it is inexact.

(To be continued).

KIMBERLEY DIAMONDS: ESPECIALLY CLEAVAGE DIAMONDS.*

By J. R. SUTTON, M.A., Sc D., F.R.S. S.A.

1. Local Characteristics.

THE difference in character between the diamonds obtained from the different Kimberley mines has been noted often enough; albeit not always in terms that convey much idea of their meaning to most people who are not directly employed in the diamond trade. Indeed, it is doubtful if mere words are competent to express the subtle shades of difference, obvious enough to the expert, between, say, a crystal from Bultfontein and one from Wesselsfontein.

One or two opinions from authorities of greater or less repute may be cited:—

"It is quite true that large parcels of diamonds from the various mines have distinctive characteristics, and it can be easily told from which mine a parcel of diamonds comes; but it is very difficult to tell in which mine a single stone may have been found, though each mine has stones in a great measure peculiar to itself." (G. F. Williams, "The Diamond Mines of South Africa," p. 492, 1902).

* From the *Transactions of the Royal Society of South Africa* viii., Part I.

"The collective character of the stones found in each mine and in each part of a mine are distinctive, but single stones of every quality occur in all mines. Thus, though it may be impossible to state the particular mine in which a single stone was found, yet an experienced Kimberley diamond merchant would have no difficulty in naming the mine, or portion of a mine, from which a parcel of stones had come, provided that the parcel formed a fair sample of the yield of that particular deposit." (Bauer, "Precious Stones," English edition by Spencer, p. 212, 1904).

1. Representative Assortment of Bultfontein and Wesselton Diamonds, in Percentages.

Size of Parcel	Bultfontein.	Wesselton.
	70,208 cts.	59,600 cts.
	Per cent	Per cent
A. Close Goods.		
Blue Whites ..	0.02	0.30
Fine Whites ..	2.06	2.64
Whites	0.55	1.16
First Capes ..	0.31	1.01
Second Capes ..	0.06	0.30
Byes	0.03	0.03
Yellows	0.03	—
First Fancies ..	1.20	—
Second Fancies ..	0.60	—
B. Irregulars.		
Whites	2.85	3.21
Capes	0.24	0.71
Byes	0.09	0.02
Yellows	0.01	—
C. Spotted Stones.		
Blue Whites ..	0.02	0.35
Whites	2.84	1.92
Capes	0.68	0.66
Byes	0.11	—
Goods	—	0.85
Good Capes ..	2.28	0.19
Second Capes ..	2.74	0.62
Darks	1.71	0.57
Dark Capes ..	0.24	—
Dark Byes ..	0.04	—
Blacks	1.52	—
D. Brown Stones.		
Light Browns ..	—	1.71
Fancies	—	0.75
Coated Stones ..	—	0.20
E. Flats.		
Whites	1.27	2.75
Capes	0.14	0.43
Byes	0.10	0.05
Greys	3.43	4.72
Darks	1.05	1.13
F. Cleavages.		
Blue Whites ..	0.14	0.04
Fine Whites ..	2.67	3.06
Fine Capes ..	0.19	0.71
Byes	0.03	—
Yellows	0.01	—
Goods	2.15	0.74
Good Capes ..	0.25	0.32
Coloured	0.70	0.74
Greys	2.70	1.61
Darks	4.31	1.17
Blacks	4.74	—
Black Rejections ..	11.09	4.43
Light Browns ..	0.22	0.42
Browns	3.15	9.46
G. Rejection Chips ..		
	—	3.65
H. Rubbish		
	23.55	27.03
I. Bort		
	18.08	20.81

2. Representative Assortment of Pool and Dutoitspan Diamonds, in Percentages.

Size of parcel. . .	Pool.	Dutoitspan.
	30,760 cts.	30,900 cts.
	Per cent	Per cent
AA. Close Goods.		
Crystals	0.07	0.44
Capes	0.07	0.26
Byes	0.13	0.41
Light Off-coloureds	0.04	0.23
Off-coloureds ..	0.11	0.04
Yellows	1.45	1.74
BB. Spotted Stones.		
Crystals }	3.20	{ 0.54
Fancies }		{ 3.01
Byes	0.27	0.77
Off-coloureds ..	0.56	0.05
Yellows	1.98	1.79
CC. Flats.		
Whites }	1.54	{ 0.07
Irregulars }		{ 2.90
Byes	0.94	0.95
Yellows	1.21	0.68
Dark Yellows ..	0.40	0.07
DD. Macles.		
Ordinaries	0.23	0.03
Darks	0.29	0.12
Blacks	1.15	1.03
Rejections	1.23	1.14
Black Rejections ..	1.11	0.46
EE. Rejection Stones.		
Ordinaries	0.13	0.83
Light Yellows ..	1.07	2.33
Yellows	0.86	—
Darks	0.76	2.23
Blacks	0.44	1.04
FF. Cleavages.		
Whites	0.62	1.05
Capes	0.75	1.33
Byes	2.19	1.23
Yellows	1.84	1.93
Ordinaries	1.07	0.77
Darks	0.42	0.77
Blacks	5.46	7.78
Rejections	0.67	2.15
Black Rejections ..	10.97	8.83
Light Yellows ..	5.78	8.00
Yellows	3.42	—
Light Browns ..	0.70	0.48
Browns	0.28	0.39
Dark Browns ..	4.81	7.00
GG. Rejection Chips ..		
	13.04	7.53
HH. Rubbish		
	19.80	15.45
II. Bort		
	8.93	10.33

Note.—Some caution must be exercised in making a first approximation to an interpretation of these percentages. It would not be fair, for example, to translate them at once into carats, and thence to argue that Wesselton produces more good white stones than Bultfontein does just because the numbers opposite "whites" are greater as a rule for the former mine. Actually the percentages of whites in the upper classes of Bultfontein are diminished because of the large number of Bultfontein white, or faintly tinted, diamonds which contain black spots—as may be seen in Class C, and especially in Class F, sub-classes greys to black rejections inclusive. Were these spotted stones (which are not numerously represented in the Wesselton yield) not in existence, Bultfontein would show the higher percentages of good whites.

"Most pipes were formed by a number of successive eruptions which gave rise to more or less well-defined columns of blue ground. Within any particular column of this nature the diamond content of the pipe rock is generally found to be remarkably uniform, but adjacent columns may differ markedly not only in their yield, but by producing diamonds of a distinctive character. So pronounced in some instances are the differences between the diamonds yielded by different columns of blue ground that experts can with [out] difficulty determine not only from which mine, but from what portion of the mine, a particular parcel of stones has been derived." (P. Wagner, "The Diamond Mines of Southern Africa," p. 149, 1914).

We propose first of all to amplify these three statements, and to illustrate them as far as it is possible to do so. Further references to the volumes in which they are contained will give the pages only, the titles will be understood.

Below are given representative assortments, in percentages, of parcels of diamonds from the Bultfontein, Wesselton, and Dutoitspan mines. Representative assortments for De Beers Mine, and for Kimberley Mine, separately, cannot well be given, since in the days when these two mines were in full swing the produce of the two was mixed together before being sorted. A specimen Pool assortment (as it is called) of De Beers and Kimberley diamonds mixed together is, however, given.

Explanatory Notes on the Assortments.

A. *Close Goods* are diamonds of good colour and symmetry and free from all blemishes of spots or flaws. In this, as in all the other classes, the sub-classes stand in the order of merit; thus a white is esteemed more than a cape, a bye more than a yellow. The sub-classes are further sub-divided into lots arranged according to size.

B. *Irregulars* resemble close goods in all respects excepting that their symmetry is inferior.

C. *Spotted Stones* resemble close goods excepting that they contain internal white or black spots.

D. *Brown Stones* are diamonds of good symmetry and free from blemishes, excepting that they have a greater or less brown or smoky hue. In the case of the light brown stones the colour is pretty equally distributed throughout the mass, as it also is in the case of the fancies (see also under A, Bultfontein) which are mainly brown. On the other hand, the smoke-brown tint of the coated stones is often confined to the surfaces, and is due to a thin deposit of opaque material, probably caused by corrosion. Coated stones are what is called "speculative" stones, since they may be good or bad inside. Pretty often they are very good indeed. They always command a good price. Bultfontein fancies differ from Wesselton fancies.

E. *Flats* differ from close goods in the matter of symmetry, namely, that their thickness is small in comparison with their length and breadth. Some of these are no thicker than a visiting card. *Macles* (for the definition of which see any standard work on crystallography) go into this class. Mineralogists and crystallographers, outside the diamond trade, commonly give the name "spinel twins" to macles. The term is not without objection, because it is calculated to make the multitude think that a macle diamond is really a spinel. It is better to confine the name "macle," in accordance with Kimberley practice, to stones in which the crystallisation has taken place right- and left-handed from a common basal plane without interpenetration from either, and to use "twin" for interpenetrating crystals.

F. *Cleavages* will be dealt with at some length later on. Here it is enough to say that the first five sub-classes—from blue whites to yellows, that is—are of good quality, colour, and shape; whereas the remaining sub-classes, from goods to black rejections, are inferior in all ways, and in the majority of individuals are spotted. Brown cleavages bear much the same relation to brown stones

that the first five sub-classes of cleavage bear to close goods.

G. and H. *Rejection Chips and Rubbish* are made up entirely of diamonds so defective in the requirements of a passable stone that no place can be found for them in any of the higher classes lest they spoil the look of the whole parcel. They comprise diamonds of all sorts other than true bort—the ragtag and bobtail of each. A good quantity of this stuff goes into cheap jewellery; much of it is used for industrial purposes, i.e., for graving tools, glaziers' diamonds, and watch pivots. Bultfontein does not produce so many small diamonds, averaging, say, a dozen to the carat, as Wesselton does, which is one good reason why it has not a class of rejection chips of its own. Such rejection chips as it has go into the rubbish.

I. *Bort* is mostly converted into powder for grinding and polishing purposes. There is a large demand for the best pieces for use in rock drills. Notwithstanding that bort only averages 5s. or 6s. a carat, really good "shot bort" will fetch as much as £4 or £5. Some of the distinctive types of bort will be described presently. Diamonds not good enough even for the rubbish go into this class.

AA. *Close Goods*. See the remarks under A.

BB. *Spotted Stones*. See C. In sorting Pool or Dutoitspan goods for the market, fancies find their best home in this class.

CC. *Flats*, here, really contain a few macles; but most Pool and Dutoitspan macles do not harmonise as well with the flats as Wesselton and Bultfontein macles do, and so we have a separate class of—

DD. *Macles* which are characteristic, in colour and shape, of the former mines. They tend to a greenish-grey, are often much spotted, and have, with few exceptions, rounded edges sloping outwards (not inwards like spinel twins) to the common basal plane.

EE. *Rejected Stones* are inferior spotted stones not good enough for BB.

FF. *Cleavages*. See F.

GG., HH., II. *Rejected Chips, Rubbish, and Bort*. The remarks under G., H., I., apply in general in these cases also.

It is to be noted that these assortments are on a strictly commercial basis. They have the market in view, and the market only, therefore they cannot fully answer all the questions that science would put; but they give useful testimony as to the outstanding points of difference between the parcels of diamonds from various sources. Roughly speaking, one system of sorting does for both Wesselton and Bultfontein, and another system for both Pool and Dutoitspan. All the same, that is not to say that for any assigned class, common to the two mines, the diamonds belonging to that class from one mine are the counterparts of those from the other. The Bultfontein cape stone, e.g., is not quite the same as the Wesselton cape. A Dutoitspan yellow has a somewhat different glow from a De Beers yellow. Bultfontein browns are sorted in with the fancies. Both they and the Wesselton browns are less full in colour than Pool browns; indeed they are smoky rather than brown. Still more diverse are Wesselton whites and Dutoitspan whites. Again, the Bultfontein yield sorts into more classes than does the Wesselton yield, there being small classes of coloured diamonds in the former which are not represented at all in the latter, which is curious, seeing that a Bultfontein parcel has quite as white a tone as a Wesselton one. As it happens, many of the yellow diamonds, and particularly the larger ones, found in Bultfontein are what is called Dutoitspan yellows; that is, they have the Dutoitspan and not Bultfontein characteristics; and this fact, coupled with the occasional find of a diamond with Bultfontein characteristics at Dutoitspan, is thought to indicate some deep underground connection between the two mines (Hatch and Corstorphine, "Geology of South Africa," second edition, 1909, 276; Wagner, 151). The superior quality of the Dutoitspan yield over that of the Pool is well

shown by the greater percentage of Dutoitspan diamonds in the upper classes. An excellent brief general account of the characteristics of the diamonds from the several mines will be found in Hatch and Corstorphine, 275, made up from notes supplied by A. Brink.

As to the denominations, it should be explained that "black" is not black in the sense in which lady novelists use the term when they rhapsodise over their heroine's priceless black diamonds. It simply means diamonds in which black spots are abundant. In Kimberley colloquial speech a black diamond is generally bort when it is not coal.

(To be continued).

BRITISH SCIENTIFIC PRODUCTS EXHIBITION, AUGUST 12 TO SEPTEMBER 7, 1918.

REPORT OF THE ORGANISING COMMITTEE.

WHEN the suggestion was made that the British Science Guild should organise an Exhibition of products and appliances manufactured in scientific industries since the advent of the war, the question of financial responsibility for such an enterprise had to be considered before any practicable scheme could be adopted. Fortunately, three members of the Executive Committee of the Guild—Sir William Mather, Sir Robert Hadfield, and Mr. Robert Mond—immediately subscribed the sum of £100 each for the purpose of taking whatever preliminary steps were desirable, even though the proposal should not be realised. On this understanding, enquiries were made of a number of leading manufacturers in typical industries with the view of determining the support likely to be forthcoming for a British Scientific Products Exhibition. The replies were so favourable that the executive Committee of the British Science Guild did not hesitate to proceed further with the undertaking; and the General Purposes Committee of the Guild was appointed, with power to add to its number, to organise the Exhibition and make all necessary arrangements connected with it.

The Organising Committee thus constituted was fortunate at an early stage in being able to secure the services of Mr. F. S. Spiers, Secretary of the Faraday Society, as its secretary. Mr. Spiers's familiarity with many industrial aspects of science, and wide acquaintance with their leading representatives, made him particularly suitable to undertake the duties of executive officer of the Exhibition; and he has fully justified the Committee's confidence. The work involved has demanded close attention for many months, and much administrative ability, both of which have been given to it by the secretary. For the first draught of the Exhibition scheme, Mr. J. H. Reynolds, formerly Principal of the Municipal College of Technology, Manchester, was responsible; and he undertook also the difficult and troublesome duties connected with the arrangement of the exhibits for several weeks before the opening. His assistance at this important stage was very valuable; and the Committee is glad to express high appreciation of it.

The central position of King's College was most suitable for the Exhibition, and the College itself proved to be admirably adapted for the display of the exhibits. Not a single complaint was received from the exhibitors, many of whom, indeed, expressed themselves highly gratified with the whole of the arrangements and the influence of the Exhibition in promoting public confidence in British scientific industry. More than three hundred different firms exhibited products or appliances representing in most cases developments during the four years of war; and, but for the necessary restrictions imposed as to machinery and certain instruments used for military and naval purposes, it would have been easy to have increased the number of exhibits many times.

Two main purposes of the Exhibition were before the Committee from the time when it was entrusted with the

carrying out of the project. One was to enlighten the public as to the capacity of British science to provide for progressive industrial expansion, and the other to stimulate further developments. It is not too much to say that the first of these objects has been abundantly fulfilled (the number of visitors was more than thirty thousand), and judging by the numerous notes made by visitors, there is good reason to believe that the second also was achieved. The attendance increased weekly from the opening by Lord Sydenham, President of the British Science Guild, to the close; and it was with regret that the Committee had to limit the period of the Exhibition to one month on account of the needs of the authorities of King's College. More than anything else the Exhibition showed that there is a large and intelligent public interested in science and its applications; and that when an opportunity is provided for them to obtain a glimpse of what has been achieved they are eager to avail themselves of it.

This interest in science and industry, when a suitable appeal is made, was shown also in the attention given to the Exhibition by the Press. The technical journals—notably *Engineering*—published numerous detailed articles upon the exhibits, and the general Press was consistently helpful in its support. The Committee realises fully that the publicity thus given assisted greatly to make the Exhibition widely known. It desires also in this connection to express its obligations to Mr. C. F. Higham for placing his knowledge and experience at the disposal of the Committee by acting as honorary director of publicity.

The thirty lectures delivered during the Exhibition provided new topics of interest every day; and the Press Bureau, under Mr. Arthur Cohen's directorship, prepared and distributed suitable notes upon them. The Committee is very grateful to the distinguished representatives of science and technology who contributed by their lectures, which were all voluntary, to the success of the Exhibition. It is hoped to publish most of these lectures in volume form, as many enquiries have been made for them.

There has been a general impression that the Exhibition was subsidised by Government; and this might have been done very appropriately if serious consideration had been given to the national value of the undertaking, which was undoubtedly very great. It is due, however, to the promoters to state that no financial aid was received from any department of the Government, though several departments were approached for a grant while arrangements were in progress. The whole of the cost has been met by donations made by exhibitors and others and by the receipts for admission. No charge was made for the space occupied by exhibits, or for the entries in the Descriptive Catalogue, the object of the Committee being to secure as representative a collection as possible independently of purely trade considerations, and to look for financial support to donors in sympathy with the patriotic motives which prompted the enterprise, whether they derived commercial advantage from the display of goods or not. The Committee is sure that all who have contributed to the Exhibition Fund will be gratified to know that their donations have effected a very useful national purpose.

While the absence of financial aid by the State must be mentioned to save misapprehension, it is with much pleasure that the Committee acknowledges its debt to the Air Ministry, which, through Brig.-Gen. R. K. Bagnall-Wild, undertook the complete arrangement of the aircraft section, and to the Board of Trade, which rendered valuable assistance by advice upon many administrative details and by the loan of a number of show cases. The two rooms devoted to the aircraft exhibits were filled with materials and objects of interest excellently arranged; and they formed one of the most popular features of the Exhibition. The thanks of the Committee are also due to the National Physical Laboratory for its exhibit of screw and other gauges and representative work in various departments of applied physics, to the Inventions Department of the Ministry of Munitions for instructive demon-

strations of the oxidation of ammonia, and to the Gas Traction Committee, of which Sir Boverton Redwood is chairman, for the interesting collection of exhibits arranged by it.

The success of the Exhibition encourages the Committee to believe that an annual display of results of British science, invention, and industry should be organised by the British Science Guild. Such an Exhibition would enable inventors to bring their devices or machines before a large public, and would provide progressive manufacturers with an opportunity of surveying all inventions likely to be of service to them as producers or users, thus serving as a kind of clearing-house for inventors and manufacturers as well as illustrating developments in science and industry. With the approval of the Executive Committee of the British Science Guild, an Exhibition of this kind is to be organised for next year, and it is proposed to use for this purpose whatever balance remains over from the recent Exhibition as a nucleus of the fund that will be required to cover the expenses of the further enterprise.

RATIONING COMMITTEE DISBANDED.

WITH the general release from Government control of raw materials used in industry the necessity for rationing disappears, and the Civil Industries Committee through whom that rationing has been exercised is now to be disbanded.

The Committee was appointed by Dr. Addison, then Minister of Munitions, in February, 1917, under the name of the Priority Advisory Committee. Its duties were to investigate the claims of industries threatened with hardship or extinction owing to the shortage of raw materials, and to make arrangements whereby they might at least be kept alive, even if not maintained at their former level. The Committee comprised some Departmental officials, but was composed mainly of business men of such standing as to give to the traders of the country a feeling of confidence that their interests would be safeguarded. The Chairman was Mr. JOHN WORMALD, of Mather and Platt, Ltd., Engineers, Manchester, and his fellow members were—

- Mr. G. E. ALEXANDER (Chairman, United Glass Bottle Manufacturers' Association),
- Mr. KENNETH M. CHANCE (British Cyanides, Ltd., Birmingham),
- Sir ARCHIBALD DENNY, Bart. (Wm. Denny and Bros., Ltd., Shipbuilders, Dumbarton),
- Mr. ALEXANDER WALKER (John Walker and Sons, Ltd., Kilmarnock),
- Mr. MURRAY WALKER (Walker Bros., Ltd., East India and South African Merchants),
- Mr. HENRY WOODALL (Director, Gas Light and Coke Company).

The Committee was housed at the headquarters of the Priority Department of the Ministry of Munitions until December, 1917, when it was constituted a Sub-Committee of the War Priority Committee, and transferred to 11, Pall Mall.

In full accord with the Controller of Priority, the Committee from the beginning undertook the rationing of manufacturers already grouped together in trade associations or capable of being grouped. It investigated the affairs of ninety-one trades, in seventy-eight of which a rationing system was established. Though its work was largely in trades dependent upon supplies of metals, it dealt also with the rationing of chemicals, oils, fats, the last named in co-operation with the Ministry of Food. In addition, the Committee from time to time, by arrangements with the Minister of Reconstruction, investigated claims made to him for materials, plant, and machinery required in preparation for the resumption of peace-time work or for the starting of new industries.

From the outset the Committee worked on the principle

of winning the co-operation of the traders themselves. No decisions were made without consultation with representatives of the industries concerned, and the meetings between the two sides were full and frank. The Committee originated the system of appointing, as official rationing authorities, independent persons of high standing, chiefly firms of chartered accountants. This system has worked to the general satisfaction of the traders rationed. To assure that the supplies of raw materials should be forthcoming, the Committee worked in closest touch with various Government departments, a close liaison has also been maintained with the War Trade Department for the purpose of co-relating manufacture to export.

The Committee has met for almost two years twice a week regularly, and in its earlier months three times a week. The Chairman, Mr. John Wormald, has given the whole of his time to the work, assisted by Mr. Frederick Simmons, and by Miss Fraser as secretary, with no other staff. For their valuable services the Committee have been warmly thanked, not only by the Government, but also by the traders whom they rationed. It is generally admitted, in fact, that this Committee has furnished a striking example of what can be effected in administration by appointing one just man of experience and of proved business ability, and by allowing him to select his own colleagues. In this way an authority was created which has done its work quietly and efficiently, and has gained the esteem and confidence of all parties. Manufacturers have seen their necessary applications reduced by a half and yet have cheerfully concurred, realising that this was the reluctant decision of sympathetic men who knew well the anxieties of management and whose life-work has been the conduct of important businesses.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 5, 1918.

Prof. W. J. POPE, C.B.E., F.R.S., President,
in the Chair.

It was announced that the Society had lost, through death, the following Fellows:—John Percy Batey (killed in action), and James Mason Crafts.

Certificates were read for the first time in favour of Pierre Beghin, 86, Market Street, St. Andrews; John Joseph Bryant, 28, Greenwood Road, Dalston, E. 8; George Butterworth, 107, Burlington Street, Ashton-under-Lyne; William Harold Squier Cheavin, 70, Somerset Road, Huddersfield; Edward Charles Cull, B.Sc., 31, Bourne Street, Dudley; John Campbell Earl, 161, South Street, St. Andrews; Algie Hancock, 3, North Street, St. Andrews; George Samuel Heaven, B.Sc., Templemead, Albany Road, Coventry; James Rintoul-Higham, Overmore, Richmond Road, E. Twickenham; Frederick William Hodkin, B.Sc., 28, Thoresby Road, Hillsborough, Sheffield; Richard Edward Johnstone, 504, Lordship Lane, Dulwich, S.E. 22; Francis Frederick Mooney, 39, Queen's Place, Summerseat, Manchester; Albert Riley, B.Sc., Westfield Lodge, Thurner, Leeds; Hugh Vernon Thompson, M.A., Croft House, Garden Village, Stoke-on-Trent; Greatrex Johnson Woods, 52, Burrard Road, West Hampstead, N.W. 6.

Mr. E. A. Evans and Capt. J. Kenner were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared duly elected as Fellows:—Lauchlan Henry Pyke Acland, B.A.; James Garfield Anderson, M.Sc.; Valentine George Anderson; William Learmouth Baillie; Frank Bainbridge; Ernest George Balls, B.Sc.; Bhaktatatar Banerjee, M.Sc.; Percy Barrs; William Andrew Stewart

Blaine, B.Sc.; Amulya Chandra Bose, B.Sc.; Louis Pierre Bosman; John Harold Bright; Hubert Thomas Stanley Britton, B.Sc.; Reginald Percy Leopold Britton; Charles Daniel Buckley; Juan Pedigo Charles Chandrasena, B.Sc.; Jules Cofman-Nicoressti; Maurice Copisarow, M.Sc.; Cyril Merton Croft; John Edwyn Davies, B.Sc.; Claude Diamond, B.Sc.; Herbert Hector Donaldson; John Edward Doodson; John Robert Douglas; George Zephirin Du Pain; Herbert John Evans, B.Sc.; Campbell Falconer; James Foster; Alfred Edwin Gates; Herbert William Gapp; Tarak Prosad Ghose, B.Sc.; Geoffrey Gladding, M.Sc.; George Grant; John Russell Green, B.Sc.; William Duthie Haigh, B.A., B.Sc.; Harry Hepworth, M.Sc.; Herbert Leslie Howard; William Claude Jago; Bernard Arthur James Jeffs; Cosmo Johns; Clifford William Judd, B.Sc.; Edwin Percy Keeble; Frederick John Kettel; Thomas Kilby; Norman Victor Sydney Knibbs, B.Sc.; Laurence Francis Le Brocq, B.Sc.; Ernest Alfred Littlewood; Shih Chen Loo; Donald Neil McArthur, B.Sc.; John Armour McKerrow, M.A., B.Sc.; Charles Stewart Maries, B.Sc.; Norman Louis Matthews; Robert Alfred Moore, B.Sc.; Albert Victor Mountford; William Newton; Douglas Norbury; Edwin Hart Nurse, B.Sc.; Mehtab Singh Obroi, B.Sc.; Leslie Henry Parker, M.A., D.Sc.; John Paterson; Wilfred Stanley Pheasey; Alexander Park Porter; Joseph Francis Pratt; Ralph John Pugh; George Thomas Purves; Dudley Ridge; George Frederick Robertshaw; Frederick Maurice Rowe, M.Sc.; Walter Salmon; Monte Ambrose Shenton; William Ramsay Sibbald; Eric Sinkinson; George Smith, M.Sc.; Thomas William Southron; Thomas Rinck Stopford, jun., M.Sc.; Joseph Tavgos, B.Sc.; William Henry Tomlinson, B.Sc.; Walter Towse; Frederick Gerald Tryhorn, M.Sc.; Henry Marshall Webb, B.Sc.; Percy William Weston; Gerald Noel White, B.Sc.; Sydney Edward Whitehead, B.Sc. Eng.; Charles Williams, B.Sc.; George Adams Pemberton Wright; John William Reginald Youll.

The following papers were read:—

"The Inflammation of Mixtures of Ethane and Air in a Closed Vessel—the Effects of Turbulence." By R. V. WHEELER.

"Blue Adsorption Compounds of Iodine. Part IV. Phenanthracoumarin." By G. BARGER and W. W. STARLING.

NOTICES OF BOOKS.

The Chemical Analysis of Iron. By ANDREW ALEXANDER BLAIR. Eighth Edition. Philadelphia and London: J. B. Lippincott Company. Pp. 218. Price 21s. net.

ALL the various methods used by the experienced analyst in the investigation of iron and steel have been brought together in this book, which is perhaps the best known of its kind and the most appreciated in the English language. The fact that it has passed through seven editions each showing some improvement in detail upon the last is sufficient to show that its value has been fully recognised. The author's wide experience and excellent judgment are both clearly revealed in the choice of methods and the clear and complete directions given for carrying them out, and no pains have been spared to assist the worker in getting really accurate results. The latest edition contains descriptions of many new methods now employed in the determination of elements present in iron and steel, and a special section is given to the analysis of alloy steels. The Ford method of rapidly determining silicon is described in detail, the section on it having been specially prepared by Mr. Ford for this volume, and the estimation of phosphorus by the method recommended by the Sub-committee on Methods of the International Steel Standards Committee of the United States is also given in detail.

NOTES AND QUERIES.

Talc, Steatite &c.—I have received enquiries regarding talc, steatite, French chalk, and shall be glad to hear if, among your advertisers, any firm can handle such enquiries and to be favoured with their addresses in the interest of international development of mineral resources.—Prof. T. CHAUDHURI, Bahampore, Bengal, India.

MEETINGS FOR THE WEEK.

TUESDAY, 21st.—Royal Institution, 3. "Lessons of the War," by Prof. Spenser Wilkinson.
— Institution of Petroleum Technologists, 5.30. (At the Royal Society of Arts). "Paraffin Wax and its Manufacture," by A. Campbell and W. J. Wilson.
WEDNESDAY, 22nd.—Royal Society of Arts, 4.30. "Meteorology During and After the War," by Col. Henry G. Lyons, F.R.S., &c.
THURSDAY, 23rd.—Royal Institution, 3. "Chemical Studies of Oriental Porcelain," by Prof. J. Norman Collie.
FRIDAY, 24th.—Royal Institution, 5.30. "One Side of War," by Temp. Lieut.-Col. Andrew Ballour, C.B.
SATURDAY, 25th.—Royal Institution, 3. "The Irish Literary Renaissance," by Rev. Canon J. O. Hannay.

Assistant Assayer (aged about 25) required by Birmingham firm of Bellion dealers, &c. Knowledge of Gold and Silver Assaying desirable. Permanent position. Good prospects. State age, experience, and salary required.—Address, "A 25" CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Chemist in charge seeks change. Metals, Minerals, Analyses; Plant control and organisation. Research (Inorganic) and new plant inception specially preferred. Good references and varied experience.—Address, "Organiser," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Junior Assistant Analyst required, between 20-22 years old, for an Analyst's Laboratory abroad. Salary and bonus.—Write, stating experience and qualifications, to C. Z., care of Street's, 30, Cornhill, E.C. 3.

Wanted immediately, Demonstrator for Chemical Department. State salary required.—Apply, Secretary, South-Eastern Agricultural College, Wye, Kent.

Works Analytical Chemist required. One conversant with Soap Manufacture, Nicotine Extractions, and Agricultural and Horticultural Preparations. State full particulars and salary required.—Address, W. A. CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

CHEMICAL SOCIETY.—FOR SALE, "Journal" and "Proceedings" of the Chemical Society, 1907-8 (bound), 1909-17 (unbound); eleven years complete. What offers?—Apply, F. C. S., 7, Bleckley Road, Bleckley, Bucks.

PATENTS AND DESIGNS ACTS, 1907-1914.

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THE CHEMICAL NEWS

VOL. CXVIII., No. 3067.

NOTES ON THE RAPID ESTIMATION OF LEAD IN BRASS AND ALLOYS.

By G. H. HODGSON.

THE usual methods described in technical books for the estimation of lead in brass and alloys serve sufficiently well for occasional determinations, but are usually too elaborate or slow for the rapid examination of large batches of work.

This has been specially emphasised during the past four years in the analytical work necessary for the inspection of non-ferrous metals used in the manufacture of component parts of high explosive shells, all such metal being subjected to a restriction on the percentage of lead permissible.

The number of laboratory tests in connection with this work was considerable, often exceeding 100 per day for any one munition area.

Of the methods in general use the electro-deposition of lead as the peroxide on the anode gives the quickest result, but was not adopted on account of the elaborate apparatus that would have been required, and also because of the limitation in the weight of sample conveniently taken for this process, and the general difficulties in the deposition which cannot be easily disposed of or controlled in routine work.

The usual volumetric methods as published and dependent upon the titration of the excess of the precipitant, or direct titration to the apparent complete precipitation point, were found to be inconvenient and unsatisfactory for general working.

The gravimetric method by fuming with sulphuric acid was largely used at first on account of its comparative accuracy, but when carried out in large batches was very objectionable by reason of the fumes evolved, and in addition the time taken to complete the analysis was far too long.

The following methods were finally adopted as being the most convenient and easy to manipulate. Both have been worked in conjunction with recognised methods for estimating lead and can therefore be considered well tested as to their accuracy.

The principal reactions are, of course, well known, but had not been adapted for a convenient and rapid working of the estimation.

The first modification consists in the initial precipitation of the lead as chromate from an acetic acid solution, converting to lead sulphate, and finally weighing as lead molybdate.

The stability of lead molybdate on ignition offers considerable advantage over the methods of weighing up direct as dried lead chromate or as lead sulphate.

METHOD I.—Gravimetric.

Time required to complete analysis about four hours. Weigh out 5 grms. of drillings (this amount is convenient for brasses containing about 1 per cent lead) into a 750 cc. conical beaker, dissolve in 25 cc. nitric acid (sp. gr. 1.4), dilute with 200 cc. of water, add 20 cc. ammonium hydrate (sp. gr. 0.88), or sufficient to precipitate the copper as hydroxide, then add 20 cc. acetic acid (80 per cent), or enough to produce a clear solution and leave a slight excess of acid. Now add 10 cc. of potassium bichromate solution (3 per cent), shake round, and allow to stand for not less than one hour.

Filter the precipitated lead chromate on to a paper-pulp pad, and wash with water to remove the bulk of the copper, and then pour on to the pad hot douches of 30 per cent sulphuric acid (about 40 cc. will be required) until the

yellow chromate is completely converted to lead sulphate, giving a final wash with cold water.

If difficulty is experienced in the conversion add a few drops of alcohol to the pad before the sulphuric acid.

The lead sulphate is then taken up in hot ammonium acetate solution (containing free acetic acid) by pouring about 40 cc. or so on to the pad and washing through into a clean 300 cc. conical beaker; bring the solution to the boil, and carefully precipitate as lead molybdate by the gradual addition of a solution of ammonium molybdate, allow to settle, filter through ashless paper pad, wash with water containing a little ammonium acetate, ignite, and weigh as lead molybdate.

Remarks.

(a) It is not necessary to filter off any meta-stannic acid formed on solution of the alloy unless present in such quantity as would interfere with the normal procedure, as it will remain on the pad after solution of the lead sulphate in ammonium acetate.

(b) Where the lead present is under 0.25 per cent the precipitation as chromate is better accomplished by adding the potassium chromate solution after precipitating the copper as hydroxide and before the addition of acetic acid. The lead being precipitated as hydroxide in the first instance considerably accelerates the formation of lead chromate on acidifying with acetic acid, and it is only so that the complete precipitation of small quantities of lead can be assured in a reasonable time.

(c) The retention of the lead sulphate by the pad during conversion from chromate is complete under the conditions described. The sulphating of lead compounds on the filter-pad is a treatment that can be used extensively to save an operation.

(d) It is essential in the precipitation of lead molybdate that an excess of the precipitant should not be added quickly, but must be added a little at a time until the point of complete precipitation is reached, otherwise acid molybdates are liable to form which would give high results.

The following are a few examples of ordinary routine work as compared with the usual fuming process:—

Sample No.	By fuming process. Per cent Pb.	By chromate process Per cent Pb.
A	2.06	2.07
B	0.433	0.433
C	0.750	0.740
D	1.50	1.49
E	1.66	1.66
F	1.63	1.64
G	0.705	0.703
Standard solution of lead and pure copper	$\left\{ \begin{array}{l} = 0.100 \\ = 0.200 \end{array} \right.$	$\left\{ \begin{array}{l} 0.100 \\ 0.200 \end{array} \right.$

METHOD II.—Volumetric.

Time required to complete estimation about two hours or less.

This method consists of the precipitation of the lead as chromate from an acetic acid solution, and titration of the iodine liberated by the chromic acid in a dilute solution of hydrochloric acid.

The operations as far as precipitation of the lead chromate are the same as in the gravimetric method described above. The lead therefore having been precipitated as chromate is poured on to a paper pulp filter and washed with warm dilute acetic acid (5 per cent) and water until free from copper salts and excess potassium chromate.

Now pour on to the pad cold 1 to 4 hydrochloric acid (free from chlorine), allow to run into a clean 400 cc. conical beaker, and wash well with cold water until all the chromic acid is completely washed through.

The solution will now measure about 150 cc. and will contain practically all the lead dissolved as chloride, which, however, will not interfere with the subsequent reactions.

The yellow chromic acid may now be titrated by the ordinary methods.

(a) Using N/10 ferrous ammonium sulphate and titrating back with N/10 potassium bichromate—using external indicator of potassium ferricyanide.

(b) Or by adding potassium iodide (10 cc. of 10 per cent solution), and titrating the liberated iodine with N/10 sodium thiosulphate, using starch as an indicator. The second method is generally the most convenient.

1 cc. N/10 = 0.0069 grm. Pb.

Remarks.

The acid used in taking up the lead chromate is important. Hot dilute sulphuric acid as used in the gravimetric process causes a reduction to chromic sulphate, while strong hydrochloric acid evolves chlorine which is partly lost during solution of the chromate.

The strength of acid 1 to 4 used cold causes no reduction as shown by the following experiments:—

	Strength of HCl used in extraction.	Titration figure.	Per cent Pb present.	Per cent Pb found.	Cc. of KI solution 10 per cent strength
1.	Conc.	9.2	1.5	1.27	3 (a)
2.	Conc.	10.45	1.5	1.44	5 (a)
3.	1-1	11.4	1.5	1.57	5 (b)
4.	1-1	11.2	1.5	1.54	10 (c)
5.	1-2	11.25	1.5	1.55	5 (d)
6.	1-2	11.30	1.5	1.55	10 (d)
7.	1-3	10.95	1.5	1.51	5 (e)
8.	1-3	10.95	1.5	1.51	10 (e)
9.	1-4	11.0	1.5	1.51	10 (e)
10.	1-4	11.0	1.5	1.51	20 (e)

(a) Solution green, reduced.

(b) 0.10 blank from iodine liberated by acid.

(c) Not good end-point.

(d) Blank 0.05 from acid. Good end-point.

(e) Good end-point. Blank negligible.

With a bulk of 150 cc. on adding 10 cc. of 10 per cent potassium iodide solution there is usually no precipitation of lead iodide, and the end-point obtained by the addition of starch is quite sharp.

The following routine results worked on the ordinary gravimetric fuming process and the volumetric method as outlined will show the excellent accuracy obtainable, in addition to which the method is clean, rapid, and can be worked in big batches.

Sample.	Gravimetric, by fuming H ₂ SO ₄ .	Volumetric, by chromate and iodine titration.
	Per cent Pb.	Per cent.
H	1.39	1.40
I	1.60	1.58
J	1.68	1.68
K	1.37	1.39
L	1.46	1.47
M	1.42	1.40
Standard solution of lead	$\left\{ \begin{array}{l} = 0.20 \\ = 0.50 \\ 1.00 \end{array} \right.$	$\left\{ \begin{array}{l} 0.201 \\ 0.500 \\ 1.02 \end{array} \right.$

M. of M. Laboratory,
Townhead Street, Sheffield.

Royal Institution.—Next Saturday, February 1, at 3 o'clock, Prof. H. P. Allen, Professor of Music, Oxford University, will deliver the first of a course of three lectures at the Royal Institution on "The Works of J. S. Bach," with musical illustrations by members of the Bach Choir. The Friday evening discourse on January 31 will be delivered by Prof. H. H. Turner on "Giant Suns." On April 4 Prof. Frederic Harrison will deliver a discourse on "The History of the City of Constantinople." The Exhibitions in the Library on Friday evenings, which were discontinued during the War, have now been resumed.

KIMBERLEY DIAMONDS: ESPECIALLY CLEAVAGE DIAMONDS.*

By I. E. SUTTON, M.A., Sc D., F.R.S.S.A.

(Continued from p. 34).

2. Comparative Statistics of Large Diamonds.

One of the most noticeable points of difference between the diamonds produced from this or that mine in the Kimberley group is in the matter of size. Taking all diamonds of 10 carats each, or greater, we have the following comparison:—

Year.	Mine	Total production in thousands of carats.	Average size of diamonds of, or exceeding, 10 carats.	Ratio of total weight of diamonds exceeding 10 carats to total production.	Number of diamonds of, or exceeding, 10 carats each in every 100,000 carats produced.
			Carats.	Per cent.	
1898	De Beers..	1897	18.2	12.25	674
1898	Kimberley..	652	17.0	11.65	684
1912	Wesseltan..	560	15.5	2.32	140
1912	Bultfontein	893	14.9	0.97	65
1912	Dutoitspan.	504	20.0	17.02	850

Thus diamonds exceeding 10 carats each in weight are relatively infrequent at Bultfontein, and average small; whereas upwards of one-sixth of the Dutoitspan yield consists of stones averaging 20 carats each.

This is remarkable, seeing that these two mines are so close together that they could even be worked (though perhaps not very profitably) from the same main shaft, and possibly have, as we have just said, some underground connection. Comparing one mine with another, the rule is essentially: The greater the average size of diamonds exceeding 10 carats each, the greater the ratio of their total weight to the total production, and the greater their number in every 100,000 carats produced. Kimberley Mine deviates slightly from the rule in the second particular.

3. Less Obvious Differences.

Besides all this there are the subtle differences, previously alluded to, between the diamonds from different mines, which, though they (the diamonds) may be called by the same name, have yet an undoubted dissimilarity one from the other made up of almost indefinable distinctions of lustre, brilliancy, crystallisation, appearance, texture, and general tone. Among other things there is the characteristic rippled surface of a Dutoitspan diamond as compared with the smooth surface, often with numerous triangular indentations, of a Wesseltan diamond, and as compared with another from Bultfontein. The passages cited at the beginning—which are not really independent statements—really understate the case. A person not in daily contact with Kimberley diamonds would naturally not be able to recognise these differences, but an expert can do so more readily than might be supposed. Single stones of every quality, it may be added, do not occur in all mines.

Slight differences have been suspected, and may indeed exist, between the lustre of diamonds won from different depths in the same mine. The evidence, however, is hardly stronger than that of mental impression based upon memory. While the expert may honestly think that the diamonds now mined are brighter, or less bright, than they used to be, there is just the possibility that his eyes may have deteriorated or his memory been at fault. Moreover, it is not practicable in the process of mining to keep the diamonds belonging to different columns of the same pipe entirely separate, and also the columns may not be of the same relative cross-section throughout, so that at one level in the mine the output may consist of a

* From the Transactions of the Royal Society of South Africa, vii., Part I.

greater proportion of diamonds from one column than it does at another level.

4. Octahedra.

The perfect octahedron is a rarity. Perhaps a few dozen have been found in the mines of the Kimberley group in forty years, and one at any rate of these was found entirely enclosed in another diamond—which suggests the possibility that any octahedron of a perfect shape, with sharp edges that is, may have spent its existence, until it reached the surface, inside another diamond. Bauer's statement that "the edges and corners of the crystals (of Kimberley diamonds) are always perfectly sharp, not even the faintest trace of rounding can be detected," is not even approximately true. Yellow octahedra are rare. The common bright yellow diamond is nearly always rounded.

5. Colours.

Orange-coloured diamonds are only found, as a rule, in the Wesselton Mine. This is curious, too, for *a priori* one would have expected to find them in mines where yellow diamonds abound, i.e., in De Beers, Kimberley, or Dutoitspan. They are practically always in misshapen fragments, like their associated minerals garnet and zircon, and doubtless owe their condition to much the same causes as wore or broke down those. They are nearly always small, not often exceeding 1 carat, and not more than half a dozen or so of them are found in a month. They keep their original colour pretty well, as a rule, after cutting. In the collection of brilliants exhibited in the Kimberley office of the De Beers Company is a beautiful rich orange-coloured diamond weighing 2 carats, cut from one of the largest of such fragments yet found. G. H. Smith's assertion ("Gem Stones," 1912, 151), that the "Wesselton Mine yields a large proportion of flawless octahedra, but above all a large number of beautiful deep orange diamonds," is perhaps approximately true as to the first half, but not reasonably true as to the second.

Pale lilac fragments are met with at rare intervals, and one reddish lilac diamond has been found and preserved, which, in shape, is like a long, flat bean, and yet has natural, though possibly secondary, faces.

Now and then stones with a greenish cast are found, chiefly in De Beers and Kimberley. They range in colour from a faint chrysolite green to sage. The lighter greens are nearly always found among rounded octahedra, and the colour appears to be concentrated in the crystal corners, and hence almost entirely disappears in the cutting, as we are told and should half expect. The sage greens are disappointing as brilliants; though they are uncommon they are not prized, for they have no life and little beauty. Steel blue and sapphire blue diamonds, like those from the Premier Mine in the Transvaal, have not been found near Kimberley.

Brown diamonds ranging in colour from smoke-brown to chocolate are found, those of the latter colour rare and precious as brilliants when they possess "fire." Beautiful pale brown and autumn brown stones, of large size up to a hundred carats but of flat and irregular habit, used to be found in the Pool. Inexperienced diggers have been known to throw them away, mistaking them for "Dutch bort" (zircon). One fine piece, worth upwards of £200, was ascertained to have been thrown away by one *débris* washer after another before it finally reached the market. Such stones cut very well. Their early history in the pipes must have differed much from that of the majority of diamonds.

After all, if the truth must be told, the common yellow diamond is far the most beautiful of all, and it would be esteemed the most if it were less common. And it has this advantage, which a good many white stones have not—that it is full of fire by day or by night. The great Tiffany lemon-yellow brilliant is a proof of this affirmation. Judging by descriptions and by glass copies, it is a Dutoitspan diamond. (The Tiffany diamond is commonly said to have been found in the Kimberley Mine in 1878.

The diamond fields newspapers of that year, however, do not report such a find).

Stones showing slight colour effects under the polariscope are not at all uncommon, but they are conceivably not so common as is sometimes asserted. The statement that nearly all Kimberley diamonds show signs of great internal strain is no more than assumption based on casual examination of a comparatively few specimens, and is scarcely more likely to be generally true than the old idea, still believed by many—that all diamonds phosphoresce after exposure to sunlight. How many South African diamonds ever go near a polariscope? (Crystals and crystallisation have always provoked random theories. Note, e.g., the old and utterly unobservant idea, endorsed by no less a philosophic autocrat than the "Encyclopædia Britannica," that "hoar frost is nothing but dew turned into ice by the coldness of the air"—3rd edition, 1897). (But see Sir William Crookes's Kimberley lecture on Diamonds, 1905).

6. Bort.

Perhaps the bort class is the most interesting of all. "Bort" as a commercial term includes inferior representatives of all the other classes besides true bort. True bort consists of crystalline aggregates of tiny particles arranged anyhow in rounded lumps. The prevailing colour is grey, and in the mass it is opaque. But very elegant cubes and spheres of this material, ranging in colour from fawn to dove, occur which are quite translucent. Typical Wesselton bort is a sort of semi-translucent substance, black by reflected light, with a lustre remotely reminiscent of tourmaline. We meet with occasional fragments of black bort, an amorphous material perhaps more nearly allied to carbonado than to true diamond. This occurs in greater abundance in the Transvaal workings than at Kimberley, and pieces have been found on the Vaal River and at Jagerfontein. It occurs in the form of irregular lumps, and is not favourably regarded as diamond at all in the market. A beautiful and unique specimen of this class, in shape generally rounded but with the corners sticking out, much like a De Beers' yellow stone in habit, is in my keeping. D. P. McDonald has described a piece of this kind of bort in "Notes on a Form of Black Diamond from the Premier Mine" (*Trans. Geol. Soc.*, S. 4., 1913). This material is known as framesite.

Bauer's statement that 90 per cent of South African bort comes from the Kimberley Mine was wrong when he wrote it, and is still more wide of the mark now.

7. Stewartite.

The most interesting and most important individual of all the very diverse bort family is the substance for which the name "stewartite" has been adopted, and which claims a section for itself. This was discovered by J. Stewart. It is of a steel-grey colour, with a dull steely sheen, and is more fibrous in texture than the types of bort mentioned above. In hardness it equals the diamond, but its specific gravity is rather less (S.G. = 3.45). It is a good conductor of electricity, like other borts. Its most remarkable property, though, is that it is magnetic and polar, and thus it has an important bearing on Crookes's theory that diamond has separated out from molten iron. Being magnetic, it must contain iron; and because it contains iron and carbon in association and is polar, we might almost call it a steel bort. Hitherto iron had only been found in infinitesimal quantities in the ash left after burning a diamond.

The properties of stewartite recall those of the fabulous, or alchemical, adamant of the Middle Ages, when a confusion of ideas (for it is difficult to conceive that there could have been an adequate knowledge of the facts) seems to have evolved an imaginary substance combining the properties of diamond and lodestone. Chaucer seems to have distinguished between diamonds and lodestones, though possibly not by intention, using the spelling

"adamauntes" for the latter and "ademauntz" for the former. Thus (Morris's ed., 1886):—

"Ryght as betwix adamauntes twoo
of evene wyght, a pece of iren isette
Ne bath no nyght to meve to no fro."
("The Parlement of Briddes").

And so in "The Romaunt of the Rose."

Whereas

"The dores were alle ademauntz eterne."
("The Knight's Tale").

Gower uses "adamaunt" and "adamant" in our sense as "diamond." On the contrary, Shakspeare uses the same word ("M.N.D." II., i) in the sense of lodestone, although his "hard-hearted adamant" has a flavour of the diamond about it.

The "Oxford English Dictionary" has an interesting article on the word "adamant," and a number of quotations from English authors down to 1750, which proves how little was known at first hand, or by experiment, of the properties of either lodestone or diamond. By many the adamant was thought to be a sort of natural opponent of the lodestone, counteracting the attraction of the latter for iron. Others regarded the adamant and lodestone as identical, and thought that the diamond was the natural opponent of both.

There is a good specimen of stewartite in the McGregor Memorial Museum at Kimberley. The substance described by Wagner (p. 143) is, of course, not stewartite at all, but black bort, the same as, or allied to, the black bort mentioned in the previous section.

8. Variation of Quality and Increase in the Output of Cleavages, with Depth of Working.

The question is often raised whether the average quality of the diamonds found in the different mines deteriorates with working depth. It is a difficult question to answer definitely, because the methods of winning the diamonds have improved with experience: so that small diamonds which might have been lost twenty years ago are now saved, and hence that the average value must decrease. In other words, the proportion of good stones to bad must decrease even if the larger ones are as good as ever they were. In the table following are given for every year 1902-16 the relative proportions for Bultfontein of—

1. Stones—i.e., Close Goods, Irregulars, Spotted Stones, and Flats;
2. Cleavages;
3. Rubbish and Bort

the mean working depth from which the diamonds were won increasing in that time from about 300 feet to 850 feet. The first column gives the years, the second the number of carats in thousands (M sorted for sale, while the others show percentages of each class.

Table Showing the Percentages of each Class of Diamonds from the Bultfontein Mine.

Year.	Carats sorted. M.	Stones. Cleavages. Rubbish and Bort.		
		Per cent.	Per cent.	Per cent.
1902-4	205	29.54	29.03	41.43
1905	291	30.84	31.87	34.29
1906	533	28.87	36.27	34.85
1907	506	26.61	35.73	37.66
1908	398	26.56	33.48	39.96
1909	670	25.05	32.01	42.94
1910	678	23.89	31.08	42.04
1911	778	23.57	35.70	40.43
1912	855	23.12	36.63	40.25
1913	787	22.25	36.30	41.45
1914-16	992	23.19	32.64	44.16

The first line is not perhaps fairly comparable with the others, since it represents the first years in which systematic work was begun by the De Beers Company, and no doubt some clearing up from previous irregular

work by various small companies had to be done. But from 1905 onwards there seems to have been a pretty clear increase, on the whole, in the rubbish and bort of about 10 per cent. At the same time the cleavages have been very little affected, while the ratio of stones has decreased from say 30 to 23 per cent. If we assume that the increase of rubbish and bort is due to improved mining methods, and reduce the ratio of rubbish and bort accordingly, this would indicate that the quantity of stones found has not decreased much, if at all, and may indeed have increased somewhat.

With this there does seem to have been an increase in the actual yield of brown diamonds as compared with the rest. The following are the separate percentages of brown and other cleavages:—

Year.	Brown cleavages.		Other cleavages.	
	Per cent.		Per cent.	
1902-4	3.92		25.11	
1905	2.96		31.91	
1906	3.45		32.80	
1907	3.85		31.88	
1908	3.91		29.57	
1909	3.52		28.49	
1910	3.84		30.22	
1911	3.88		31.82	
1912	4.15		32.48	
1913	4.28		32.02	
1914-16	4.38		28.26	

Whether any of this result is due to psychological reasons is hard to say. Diamond coloration merges from one class to another not by steps but imperceptibly. And it might therefore be plausibly urged that some cleavages which formerly were not brown enough to be called brown are now so called; or that it is likely that improving markets have to some extent justified the promotion of individuals from the rubbish into the brown cleavages. Neither alternative has any trustworthy evidence in its favour, and my own impression is that the increase in the brown cleavages is real, the small deviations from a uniform increase showing no definite relationship to the deviations of rubbish and bort.

The next table gives similar information for Wesselton for the years from 1898 to 1916—namely, the relative proportions of—

1. Stones—i.e., Close Goods, Irregulars, Spotted Stones, Browns, and Flats;
2. Cleavages;
3. Rejected Chips, Rubbish, and Bort;

the mean working depth from which the diamonds were won increasing in that time from 125 feet to 800 feet.

Table Showing the Percentages of each Class of Diamonds from the Wesselton Mine.

Year.	Carats sorted. M.	Stones. Cleavages. Rubbish and Bort.		
		Per cent.	Per cent.	Per cent.
1898	378	31.72	17.06	51.22
1899	447	29.53	15.47	55.00
1900	308	28.14	15.51	56.35
1901	484	28.08	16.33	55.59
1902	541	26.65	17.76	55.59
1903	580	25.97	17.86	56.18
1904	612	23.86	19.20	56.93
1905	567	24.98	19.39	55.63
1906	590	24.41	20.56	55.03
1907	472	26.81	23.67	49.52
1908	397	25.95	23.86	50.19
1909	618	25.56	24.72	49.72
1910	525	25.81	25.61	48.57
1911	409	24.39	23.43	52.18
1912	522	24.17	24.87	50.96
1913	602	23.05	25.20	51.75
1914-16	634	23.38	23.05	53.57

Here we find, so far as the statistics can show it, a decrease in the percentage of stones of about 7 per cent (about the same as that of Bultfontein in a little shorter time); an increase of cleavage of about the same amount; and a remarkable fluctuation in the percentages of rejection chips, rubbish, and bort, the curve of these showing, on the whole, a maximum in 1904, followed by a minimum in 1910, and after that a rise to the present time.

Curiously enough, the brown stones show a uniform decrease with time, whereas the brown cleavages show a definite increase, thus—

Year.	Brown Stones. Per cent.	Brown Cleavages. Per cent.
1898	2'82	5'17
1899	3'10	6'35
1900	2'97	6'44
1901	3'55	6'20
1902	3'33	7'15
1903	3'14	7'22
1904	2'62	8'19
1905	2'49	7'63
1906	2'37	8'21
1907	2'65	9'65
1908	2'29	9'61
1909	2'28	10'70
1910	2'17	10'84
1911	1'97	9'64
1912	1'89	10'13
1913	1'90	10'57
1914-16	2'12	10'13

This is an extraordinary result, and requires more material for its full elucidation than has yet been accumulated. It would appear from the face value of the relative numbers that brown stones have shown a greater disposition to break up in the deeper levels of the Wessellon Mine than in the upper ones. Also that brown diamonds (stones and cleavages together) have increased by about 3 per cent in eighteen years, the fluctuations showing some, if small, agreement with those of rejection chips, rubbish, and bort.

Comparing stones other than brown with cleavages other than brown, we have—

Year.	Stones not brown. Per cent.	Cleavages not brown. Per cent.
1898	28'89	11'89
1899	26'43	9'12
1900	25'17	9'07
1901	24'53	10'13
1902	23'32	10'61
1903	22'83	10'64
1904	21'24	11'01
1905	22'49	11'76
1906	22'04	12'35
1907	24'16	11'02
1908	23'66	14'25
1909	23'28	14'02
1910	23'64	14'77
1911	22'42	13'79
1912	22'28	14'74
1913	21'15	14'63
1914-16	21'26	12'92

Here we see that there has, apparently, also been a disposition for these whiter diamonds to break up more freely at the greater depths, although not to the same extent as in the case of the brown diamonds. For whereas in the five years 1899-1903 67 per cent of all brown diamonds was brown cleavage, in the five years 1909-13 the cleavages had increased to 84 per cent, an increase of 17 per cent, the corresponding percentages for diamonds other than brown being 29 and 39, an increase of 10 per cent. Moreover, in absolute numbers, the chances preponderate that a brown diamond will be a

cleavage, whereas the odds are quite the other way when the diamond is not brown. There is pretty well as much brown cleavage as there is cleavage not brown; the stones other than brown outnumber the brown stones by ten to one. Bauer, in one of his characteristic inaccuracies, has stated that in the case of Cape diamonds "it is a remarkable fact that these cleavage fragments are nearly always white—that is, colourless, or, at least, very faintly coloured; fragments of a dark colour, or of a decided yellow, are extremely rare, so that we must conclude that such stones offered greater resistance to fracture than did the colourless diamonds" (p. 209). The above statistics show just the opposite—that it is the colourless diamonds rather which resist fracture, as compared with brown, at any rate, although, as we shall see when we come to speak of Pool and Dutoitspan diamonds, yellow diamonds are perhaps more resistant than white. Apart from any question as to the influence of colour upon the cohesion of a diamond, we should naturally expect cleavages to appear somewhat lighter in colour than stones, for the same reason that many cut diamonds appear lighter in tint than they did when in the rough. A good deal of the colour in some rough stones seems to be concentrated in the crystal corners from which it is reflected inwards, so that if the stones were to be broken the fragments would assume a lighter tint. We have also to remember such a fact as that the deepest coloured glass appears lighter in colour when broken into small enough fragments, and quite white when reduced to powder. Diamonds may look lighter in colour because they are broken; they do not break because they are lighter.

9. Cleavages.

One point to be noted concerning what are called cleavages is that some of them are not broken diamonds at all. Wodiska's statement ("A Book of Precious Stones," 1910) that "cleavage" means broken stones is too uncompromising. "Cleavage" is a trade term which indicates not only diamonds now broken, but those which will have to be broken before being finally cut into gems—potential cleavage, in fact. All very misshapen stones and interpenetrating crystals, besides broken pieces, are cleavages in the eyes of a Kimberley diamond merchant, just as all flesh is grass, and so are feathers too, in the eyes of the philosopher. Bultfontein produces numbers of these interpenetrating crystals, or cross-grained stones, as they are called. Some of them take strange forms. A fine white one in my collection is like two mace-heads, with sharp, projecting points, joined together. The term "cleavage" does not apply, however (as Bauer says it does), to crystals containing spots which would have to be cleaved before being cut. A crystal containing spots is a "spotted stone," and is dominated dark, black, or black rejection, according to its quality. Some of these so-called cleavages have evidently crystallised in a tight corner, judging by their distorted outlines and by the fact that sporadic specimens appear to have surfaces of attachment like quartz. Others appear to have been broken at an early stage, and to have undergone further growth or suffered resorption. It is truly remarkable how many of these so-called cleavages seem to have been naturally refaced either with a nascent or with a pocky surface. The triangular indentations indicating growth—so common on the faces of Wessellon octahedra—do not, nevertheless, seem to occur on these naturally renovated cleavage faces; instead, striations like those on yellow diamonds are the rule.

(To be continued).

Gas from Straw.—It is reported from Saskatoon that the Advisory Council of Scientific and Industrial Research is establishing a plant near the city for experiments to be made during the coming winter on the production of gas from straw.

THE CONFIGURATIONS OF ORGANIC COMPOUNDS AND THEIR RELATION TO CHEMICAL AND PHYSICAL PROPERTIES.*

By ARTHUR MICHAEL.

(Continued from p. 31.)

The Relations between the Chemical Properties and the Configurations of Unsaturated Acids.

Addition.—In unsaturated acids the additive relationships to structure and stereo-structure are identical. Velocity of addition depends on the quantity of the free energy that is manifest at the unsaturated carbon atoms or at the carbonyl group, and on its quality in respect to that of the components of the addenda; reactive capacity on the sum total of the free and bound energy and chemical affinities that there come into play, which constitute the chemical factors entering into the entropy increase (43).

The affinity values of the unsaturated carbons should vary with the chemical nature of the other elements in the molecule (*Journ. Am. Chem. Soc.*, 1910, xxxii., 995), and the magnitude of this influence should accord with their spacial positions to them, and should be indicated in the "scale of combined influence" (*Ibid.*, 1910, xxxii., 999; 1912, xxxiv., 849; 1918, xl., 708). Furthermore, the nature of their effect should be to change the affinities of the Δ -carbon atoms in the direction of their own values to the addenda, and owing to the "chemical plasticity" of carbon its free energy must be extremely susceptible to such influence (*Journ. Am. Chem. Soc.*, 1910, xxxii., 995). Substituting a hydrogen in ethylene by an acid radical containing oxygen changes the affinities of the Δ -carbon atoms in the direction of those of the latter element; i.e., it reduces the values for halogen, although it increases their free energy. The resultant of such a structural change is to diminish the addition velocity and the addition capacity for halogen in proportion to the affinity constant of the acid whose radical is introduced, and to the number of such groups. This influence is greater in unsymmetrical than in symmetrical substitution, as the change in affinity values of a single Δ -carbon must be the dominating factor in determining the velocity and capacity of halogen addition.

The accumulation of such acid radicals, or even a single one when it is so negative as NO_2 , at a Δ -carbon atom may reduce its affinity value for halogen to practically nil, and addition will not take place. Corresponding replacement by alkali increases the affinity of the Δ -carbon atoms for halogen, but decreases their free energy; both of the changes are in proportion to the positivity and number of the groups introduced (Michael, *Journ. Prakt. Chem.*, 1899, [2], lx., 432). Substitution in this case results in an increased velocity of reaction, but a number of very positive radicals, like the tertiary alkyl groups (*loc. cit.*, 423, footnote 4; 1901, lxiv., 107; *Ber.*, 1906, xxxix., 2790), through the reduction of the free energy in the Δ -carbons atom, may result in practically no change or even a falling off in the velocity.

The shifting of the unsaturation from the α,β - to the β,γ position removes the Δ -carbons from the 3,4 to the 4,5 place from the oxygens, and, since 3 is much more important than 5 in the "scale," the velocity of halogen addition in monobasic acids with similar configurations is greatly increased (Sudborough and Thomas, *Journ. Chem. Soc.*, 1910, xcvi., pp. 714, 2450). Methyl introduced into acrylic

acid in the β -position, i.e., $\overset{3}{\text{CH}_3}$, to the oxygens, reduces the negativity of that element more when it is in the *cis* than in the *trans*-position, and in accord with this relation is the greater addition velocity of allocrotonic over crotonic acid.

This accelerating influence of *cis*- over *trans*- $\overset{5}{\text{CH}_3}$ is again shown in the larger values of angelic acid (19×10^{-5}) over tiglic acid (9.9×10^{-5}); β -dimethylacrylic acid (700×10^{-5}) shows a very large increase, owing to both the methyl groups influencing the same Δ -carbon atom, and a further great augmentation occurs in trimethylacrylic acid (2200×10^{-5}), which is due to the strong

positive influence of the $\overset{4}{\text{CH}_3}$ on the oxygens. As would be expected the extent of the influence of the methyl group is modified with larger primary alkyl groups, but not the relative relations in the homologous stereomeric derivatives; thus the mal. oleic and erucic acids add bromine with greater velocity than the respective fum. derivatives (Sudborough and Thomas, *loc. cit.*).

The influence of bromine and methyl on the additive capacity for bromine in acids of the type $\text{R}_2\text{C}=\text{CR}(\text{COOH})$, has been treated by Bauer (*Ber.*, 1904, 3318, xxxvii.), who gives the rule that addition occurs until R is entirely replaced by Br, or Br with ("neben") methyl (44). Perbromoethene decomposes on heating into perbromoethylene and bromine (Merz and Weith, *Ber.*, 1878, xi., 2239), and since replacing a Br in the latter body by carboxyl greatly diminishes the affinity of the Δ -carbon atoms for halogen, the inertia of tribromoacrylic acid accords with theory. Replacing a halogen in this acid by methyl should facilitate addition, and that substitution and not addition products have been obtained from the stereodibromocrotonic acids (Pinner, *Ber.*, 1895, xxviii., 1877), is probably due to the replacement of the methyl hydrogen atoms by halogen preceding easier, under the conditions of the experiments, than halogen addition.

The addition velocities of such bromo-acids have not been investigated. In acids of the same group a mono- α -Br derivative should unite less readily than either of the stereo- β -products, as in it the retarding influences are both exercised on the same Δ -carbon atom; and in the latter compounds the *trans*-easier than the *cis*-form. Further, the effect of replacing hydrogen in these acids by alkyl should be to accelerate the velocity in the order of *trans*-, *cis*-, and α -substitution.

The affinity of nitrogen for bromine is also extremely small, but that CN reduces the additive capacity more than $\text{COOC}_n\text{H}_{2n+1}$, in the same position to the Δ -carbon atoms (Bauer and Moser, *Ber.*, 1907, xl., 919; *Journ. Prakt. Chem.*, 1905, [2], lxxii., 201), is the result of the partial neutralisation of the negative energy in the oxygen atoms by the positive alkyl group. This effect shows itself, too, in the easier additivity of the esters under comparable conditions over the corresponding Δ -acids, which should increase with the relative positivity of the alkyl group.

In several addition reactions with compounds whose Δ -carbon atoms show but slight additive capacity for bromine, a balanced reaction has been observed (Bauer and Moser, *loc. cit.*), which is due to the affinity of the solvent employed for the halogen. Indeed, the preliminary formation of a "polymolecule" of halogen and solvent undoubtedly precedes the addition in some cases, which explains the sometimes observed dependence of the velocity on the solvent, notwithstanding that the compound and the addition product are both in solution.

It is generally accepted that the fum. modification of the dibasic, α,β,Δ acids shows a smaller addition velocity for halogen than the mal. form, but since the insolubility of a Δ -acid as well as that of the product of addition are large deterring factors (Michael, *Journ. Prakt. Chem.*, 1895, [2], lii., 291), and they are usually greater in the fum. product, no sure conclusion is furnished by the available experimental data. According to Anschuetz (45), (*Ber.*, 1879, xii., 2282), the esters of maleic and fumaric acids, whose energy relations (see under "Density") and physical properties are much closer together than those in the acids, add bromine approximately with like readiness,

* From the *Journal of the American Chemical Society*, xl., No. 11.

even with the methyl esters where the *fum.* form is a solid and the *mal.* derivative is a liquid.

A comparable though smaller approach in the energy contents and in the physical properties takes place in the dibasic acids with the replacement of a nuclear hydrogen atom by an alkyl group, and accordingly the additive velocities of such derivatives lie closer together than those of the mother substances.

Since citraconic anhydride and mesaconic acid unite readily in sunlight with bromine, an increase in the addition capacity with nuclear methylation is indicated theoretically. In reality dimethyl-maleic anhydride and dimethyl-fumaric acid do not unite at all with bromine (Fittig, *Ann.*, 1898, ccciv., 117). The spontaneous anhydridisation of dimethyl-maleic acid has been explained as resulting from the apical approach of the axial Δ -carbons, which must also occur in dimethyl fumaric acid, and it is possible that this slight apical distance may be a deterring factor (Bischoff, *Jahrb. Chem.*, 1890, i., 176).

Although the anhydride does not add bromine the methyl ester of the corresponding acid does so readily (Baeyer, *Ann.*, 1890, cclviii., 162), and the anhydride itself unites with chlorine (Michael and Tissot, *Journ. Prakt. Chem.*, 1893, [2], xlvii., 382; 1895, lii., 340). These facts do not necessarily conflict with the above view. On the one hand, the chemical nature of the ester gives its axial Δ -carbons greater additive power than those in the anhydride and their segmentation is less, and, on the other hand, chlorine has not only more free energy and a greater affinity for carbon than bromine, but a smaller atomic volume.

Alkylene iodides decompose readily with loss of the halogen. The replacement of a hydrogen by carboxyl adds to this instability, and in a direct relation to the apical distances of the oxygen atoms from the carbon atoms joined directly to the iodine. This reduction of the affinity value is so great with the α, β, Δ -carbons in ethylenic acids as to render such addition products unstable under ordinary conditions; i.e., these acids do not unite with the halogen (46).

It may seem anomalous, therefore, that the α, β -acetylenic acids are able to add iodine (Liebermann and Sachse, *Ber.*, 1891, xxiv., 412 and 2588; Bruck, *Ber.*, 1893, xxvi., 845); although very much less readily than chlorine and bromine. There are several reasons for this exceptional behaviour. First, iodine shows a greater affinity than chlorine for oxygen, and a further decrease is shown by bromine (47); the carboxyl must therefore relatively decrease the affinity values of the completely Δ -carbon atoms for the halogens, inversely in the order named, since there is no hydrogen joined directly to them to offset these affinity relations. Second, the affinity of carbon for halogen increases with unsaturation (*Journ. Prakt. Chem.*, 1900, [2], lxi., 448), which is undoubtedly connected with the accompanying increment in the free energy (48).

Elimination.—The writer (*Journ. Prakt. Chem.*, 1895, [2], lii., 289; *Ber.*, 1901, xxxiv., 4221) showed experimentally that the relative ease of addition of halogens and halhydric acids to unsaturated derivatives, and the elimination of the addenda from the addition products, stand in a direct relation, even when stereomeric compounds are involved in the reactions. A theoretical foundation of these relations is possible in the dibasic acid series, but is less evident for monobasic derivatives, and the question will not be considered in this paper.

Werner ("Lehrb. d. Stereochemie," 1904, p. 210) believes that the relation could have been foreseen from Ostwald's (49) "law of reaction stages" ("Grandlinien d. Anorg. Chem.," 1900, p. 215), according to which the least stable of the possible reaction compounds is always primarily formed. The direct formation of fumaroid addition products from acetylenic derivatives and halhydric acids or bromine, not to mention other facts, renders such a conclusion untenable, as they also do Ostwald's supposed law.

According to J. Wislicenus the addition of halogen to ethylenic, stereomeric compounds, and subsequent elimination of halhydric acid from the addition products, with the acceptance of *cis*-processes, leads to an inversion in the stereomeric types. Notwithstanding that such *cis*-processes, generally speaking, have long since been experimentally disproven, and also that attention was called to the fact that the intraconversion of the *mal.* into the *fum.* derivative, and *vice versa*, was not dependent on the above theoretical explanation (Michael, *Journ. Prakt. Chem.*, 1895 [2], lii., 362), such stereomeric reactions are still frequently quoted as evidence in favour of Wislicenus' views (50). As far as has been investigated all such additions to stereomeric ethylenic compounds are *trans*-processes, as also are the eliminations of halhydric acids from the addition process (Michael, *loc. cit.*; *Journ. Am. Chem. Soc.*, 1918, xl., 714). These relations were clearly indicated in the behaviour of the acetylenic compounds, where the additions are largely or completely *trans*-processes, and where *trans*-eliminations proceed more readily than *cis*-processes, since the intramolecular shifting of atoms or groups, which is involved, experiences greater hindrance in them than in the less unsaturated ethylenic derivatives.

Notes.

43. If a solvent is used, and it enters into the composition of the "polymolecule," it may radically influence both factors, but especially the velocity (Michael and Hibbert, *Ber.*, 1908, xli., 1091).

44. The latter statement is too vague and broad; it may be correct if changed to read Br and one β -methyl. Perbromomethylacrylic acid should add bromine.

45. Unfortunately no quantitative data on this interesting subject are known.

46. It is probable that the monobasic ethylene β, γ - and γ, δ acids are capable of adding iodine. If so, the first derivatives should unite somewhat more readily, and their addition compounds should show less instability towards heat than the isomeric products from the latter acids.

47. For this reason, and because of its greater free energy and larger affinity value for carbon and hydrogen, chlorine should require more carboxyl or nitrile groups than bromine to prevent addition. The difference in the behaviour of such relatively quite negative carbon towards these halogens is characteristically shown by CO. Probably all or at least most of the unsaturated compounds that are inert towards bromine should be capable of uniting with chlorine.

48. The relations in the addition of halhydric acids to Δ -acids will be treated in a separate paper, in connection with the influence of solvents on the course of the reactions, which has been reinvestigated experimentally.

49. The statement of facts in the form of a rule is not an explanation, as Ostwald supposes, and the reactions advanced in its support, e.g., the preliminary formation of hypochlorites and the products of progressive oxidation, leads one to believe that he not only overlooked Dalton's atomic theory, but that each salt is formed alone under given experimental conditions. The "rule" is illustrated graphically by steps leading to the highest product of oxidation, and the statement is made that "a further step ('Stufe') between chlorate and oxygen is realised when $KClO_3$, or another chlorate, is carefully heated." This reminds one of S. C. H. Windler's (*Ann.*, 1840, xxxiii., 308) famous conversion of $Mn(C_2H_3O_2)_2$ into $Cl_{24}.H_2O$, and Ostwald was unaware that most chlorates do not yield perchlorates.

50. For instance, in Stewart, "Stereochemistry," 1907, p. 182; Meyer-Jacobson, "Lehrb. Org. Chem.," 1910, i., 487; also in numerous papers in chemical literature.

(To be continued).

SCIENCE AND THE FUTURE.*

By ALAN A. CAMPBELL SWINTON,
F.R.S., M.Inst.C.E., M.I.E.E., M.I.Mech.E.

(Continued from p. 27).

THE importance of provoking an interest in scientific subjects is paramount, and once the interest is created those interested can follow matters up in particular spheres by special reading. What is wanted is to awaken a taste for scientific literature, after which the pursuit of the fairy tales of scientific discovery and invention will by many be found much more fascinating than the literary rubbish upon which so large a majority of the population flitter away their time.

Though, according to the testimony of experience, great inventors are born and not made, the creative power of inventors, at any rate in its highest form, being a natural gift which cannot be acquired by any amount of study, still with the increased spread of scientific knowledge that suitable education must bring about, invention is bound to benefit greatly. For one thing, persons gifted with inventive genius, who without scientific knowledge would only be able to apply themselves to comparatively simple problems, will with the larger vision that a good scientific education will give, keep off the impossible projects on which some quite ingenious, but uneducated, inventors waste their energies, and will be anxious and able to tackle questions which otherwise would never have come within their purview. To this end, however, the education must be suitable in kind and not of such a description as by too much learning is apt to cramp originality. Again, with more knowledge persons may find that they possess inventiveness, who otherwise would never have made this discovery. As regards scientific research and discovery, the case is perhaps more simple, as much useful research can be carried on by persons who are destitute of any high degree of origination faculty—painstaking and methodical powers of observation, which can certainly be developed by training, being the chief requirements for much of the work. For great generalisation and discoveries of the first order, the highest degree of intellect will no doubt still be requisite, but it is hoped that with the increase of knowledge a greater number of persons will find that they possess these natural and unacquirable attainments.

There is a fallacious notion abroad that practically all great scientific work has been done by the poor. No doubt necessity is the mother of invention, and poverty in every walk of life often acts as a considerable incentive. So far as the facts are concerned, however, let us remember that at least two of our greatest scientific discoverers, namely Robert Boyle and Henry Cavendish, were the possessors of great inherited wealth, and that there are other instances of a similar character. Indeed, but for their wealth and the leisure that they thereby enjoyed, not a few of our most eminent men of science would probably never have brought their labours to fruition, while there are many instances of inventions that could only have been made by persons who had the command of much money. James Watt could never have accomplished what he did without the wealth of his partner Boulton, and to come to more modern times the development of the steam turbine, which entailed years of costly experimenting without any adequate financial return, is another case in point. It is the old story of one man's meat being another man's poison. Some temperaments require the spur of necessity to make them exert themselves while for others the grinding task of providing daily sustenance for themselves and their families suffices to exhaust their energies and leaves nothing for other endeavour. In the literature of Industry we frequently come across accounts of the poor inventor who, though almost starving, by superhuman endurance and perseverance eventually

achieves success. We hear nothing, however, of the countless others in whose cases "Chill penury repressed their noble rage, and froze the genial current of the soul." If poverty may be deleterious in the case of individuals, it is still more so when we come to consider larger units such as whole industries, and there can be no more sure fact than that no industry is in a healthy condition, or is likely to advance and increase, which does not make good profits.

Just as John Stuart Mill feared that the limited number of notes in the audible musical scale would in time lead to the exhaustion of all possible melodies, so there have been those who have thought that scientific discovery would before long come to a stop owing to the dearth of subject-matter and to the limitations of the human intellect. Whatever may be the fact in regard to music, nothing could be more erroneous than this idea in respect to Science, for the reason that every new discovery and invention opens up the path for others, and thus the scientific horizon surely widens year by year. Indeed, so far from discovery and invention being likely to come to a stop, both are sure to extend at a rapidly increasing rate, particularly if we have more Science taught to young people and greater encouragement given to scientific workers with consequent addition to their numbers. In the comparatively new fields of radio-activity, electromagnetic radiation, synthetic chemistry, chemical catalysis, electrical osmosis, photo-electricity, and corpuscular matter, to mention at random only a few of those that readily occur to one, the prospect seems practically illimitable. Moreover, new materials with new properties, whether elementary substances such as the new gases—Argon, Helium, Krypton, Neon, and others; the so called rare earths—Thorium, Cerium, Yttrium, Scandium, and the rest; or new alloys and compounds which chemists and metallurgists keep providing for particular purposes, afford fresh means for pursuing research. We have also new mechanical appliances of all sorts, and new methods which enable us to obtain on the one hand, in the electric furnace, temperatures approaching in heat to that of the sun, and on the other hand in special refrigerators to cold quite near to that of space and of the absolute zero—temperatures both high and low, quite beyond reach only a few years ago. Again we have learnt how to apply prodigious mechanical pressures and how to obtain gaseous vacua on unprecedented scales. We can produce and employ electric currents and pressures, and both electric and magnetic fields, of intensities previously unknown, and measurements of all kinds can be made with a delicacy and an accuracy almost beyond belief. The number of these things is much greater than there is time to record here, and their importance is intensified by the fact that each reacts on the others with the production of more, so that the tools and agents at the disposal of research are continually being added to. Nor, if we turn from pure science and its possibilities and means for discovery to inventions and the science that is applied to utilitarian uses, is the case in any wise different. Here again the effects are cumulative, both discovery and invention assisting to bring still further invention within our reach. The petrol engine, originally invented for propelling boats, and later adapted to driving land vehicles, has rendered possible the conquest of the air by the aeroplane, as also the depths of the sea by the deadly submarine. Bell's telephone, that instrument of almost sublime simplicity, which, as originally produced, was intended for transmitting speech, is now used for receiving the inarticulate signals of wireless telegraphy, which could hardly have reached its present development without it. Photography and its sensitive plates and papers are now applied in radiography and in other directions of which the original photographic inventors never dreamed. The metal cerium first brought into notice by its being a necessary constituent of incandescent gas mantles, now in pocket lighters helps the smoker in these difficult times to dispense with matches. The vacuum jacket, invented by Sir James Dewar for keeping liquid air cold, is used to day for

* An Address delivered at the opening meeting of the 165th Session of the Royal Society of Arts on November 20, 1918. From the *Journal of the Royal Society of Arts*.

keeping things hot. Radium, which when discovered by Madame Curie was only a scientific curiosity, has many applications in medicine, and is now used to illuminate watches and instrument dials so that they can be read in the dark. The gyrostat, which is a development of the child's spinning-top, and used to be merely a scientific toy, is now the foundation of a description of ship's compass, which points to the true and not to the magnetic north pole of the earth, and without which the navigation of submarines would be almost impossible. Tungsten, which a few years ago was unknown in true metallic form, now constitutes the filaments of all our incandescent electric lamps, while the discoveries of Crookes, J. J. Thomson, and others in connection with rarefied gases have rendered possible the so-called half-watt lamp of surprising efficiency. By an electric process as old as the time of Cavendish, who discovered it, nitrogen from the air is now being extracted to make nitrates so necessary for agricultural fertilisers and for explosives, which latter have their uses apart from their application to warfare. The cinematograph of the modern picture palace has developed out of the old wheel of life of the days of our childhood. Indeed the list that could be compiled is almost endless.

One of the most interesting of modern inventions is that of wireless telegraphy, and it is also one which appears to present great scope for improvement and extension. There is a mysterious fascination that captivates the imagination about these wireless signals, which come over hundreds and thousands of miles of space without any visible or tangible means of connection. Yet, as a matter of fact, they are in nowise more wonderful than telegraphy by wire. Indeed, had, as might quite have been possible, the wireless method been the first to be discovered, then our wonder would have been excited at the ease with which by means of a wire of minute section, the signals could so easily be conveyed over prodigious distances in any direction to any required point. For the wireless system is really analogous to the uproarious fog-horn, whose signals are sent out far and wide in all directions, for all who have ears, and are within range of the sound, to hear; while wireless telegraphy more resembles the speaking-tube, whereby much smaller sounds are conveyed from the speaker to a particular listener at the other end.

Now during the past five years the improvements made in wireless telegraphy, and also in wireless telephony, have been very important, but as yet it is not admissible to discuss them; besides, my subject is rather the future than the past. One matter, however, is within public knowledge, and that is the increased and still increasing amount of news that we get in the papers that appears under the heading of "Per Wireless Press." Indeed wireless telegraphy appears to be developing at last in what has always appeared to me to be its proper field, which is not so much to communicate between one individual and another, but rather for the communication of intelligence broadcast over the earth, "*Urbi et Orbi*"—to the city and to the world—to borrow from the famous wording of the Papal benediction from the Loggia of St. Peter's in Rome of bygone times. No doubt maritime wireless communication between ships, and between ship and shore, hitherto its most useful application, is another case altogether, and supplies a want that telegraphy by wire cannot meet at all. With this we are already familiar, while the use of wireless as a voice that can speak simultaneously to points on every portion of the earth is in some ways a more novel proposition.

No doubt some persons who had private wireless stations of their own before the war, were used to getting time signals from Paris from the Eiffel Tower, and from Nauen in Germany; while a few of those who had mastered the difficulties of reading the Morse alphabet by ear, were able to decipher whether reports from these places, as well as from our own Admiralty, in addition to general news from Poldhu in Cornwall, and from one or two other large stations.

What I have in my mind, however, goes much farther than this. In London tape and column-printing telegraph instruments operated by wire, that record sporting, parliamentary, and general news, have long been familiar objects in clubs and hotels, and have become a portion of our daily life. Now there is no reason at all why similar printing instruments, which he who runs can read, should not be operated by wireless means, not only in London and other large cities, but throughout the country, or even throughout the world. Special transmitting stations using different wave lengths could send out the messages, while separate printing machines, tuned each to respond to the wave length of a particular transmitter, at each required point, would receive and record them. No connecting wires, costly both as regards first expense and as regards upkeep, would be required, but only suitable aërials at each transmitting and receiving station.

Some regulations would be necessary to prevent interference, and as wireless waves, travelling as they do through the ether of space at the enormous speed of 186,000 miles per second, recognise no international boundaries, they would have to be universal. Thus arises a fitting opportunity for the League of Nations. For the distribution of news to the press nothing could be better or more economical, while there is no reason why clubs, hotels, and private houses everywhere should not also be thus supplied with the latest intelligence. For in wireless telegraphy it costs no more to send signals to a thousand receiving stations than to a single one, and there is practically no limit to the number of the stations that can simultaneously receive signals from a single transmitting station. To some, this sketch of the universal distribution of news to all and sundry may appear fantastic, but it is not really so at all; for, at any rate as concerns an area no larger than Western Europe and the British Islands, it is well within the range of practicability at the present time, and only requires a little working out to arrive at the best arrangements. Nor is this all: spoken words of the human voice have already been intelligibly transmitted by wireless across the Atlantic between the United States and Paris, a feat that has never been accomplished by cable; and there is no reason that I am aware of, why, in the near future, we should not have a public speaker, say in London, in New York, or anywhere, addressing by word of mouth and articulate wireless telephony an audience of thousands scattered, may be, over half the globe.

Great things are at present being foretold as to the marvels that we are to see in the way of the electric distribution of energy throughout the whole country from a small number of giant generating stations. Indeed, the subject is considered of sufficient importance to be mentioned in the Prime Minister's election address, which in itself is surely a sign of the times. The hope is held out that electric energy is thus to be so cheap that it will supersede every other kind of energy, not only for driving our mills, our machinery, and our railway trains, but also universally for cooking, heating, and other domestic purposes. Great improvement over our present parochial methods according to which Parliament, in its wisdom, has divided up the country into an enormous number of absurdly small municipal electrical areas, which are far too limited in consumption for any reasonable economy to be obtained—is no doubt possible, but let us not be too sanguine. Some of the highest and most experienced authorities are of the opinion that the limits of economical generation and distribution are already being reached in the case of some of our larger systems, and that when we get above tens of thousands of horse-power, the step in hundreds of thousands does not effect more than a small percentage of saving, either in first cost, or in cost of working. There is also the question of material for the distribution conductors. Excepting silver, which of course is out of the question, pure copper, which is almost as good as silver, is the best electrical conductor we know of, and the amount of copper in the world is of course

limited. No doubt by raising the electrical pressure, the amount of energy conveyed through a given conductor with a given loss, can be largely increased. But again there are limits to the endurance of insulating materials that can be obtained at a reasonable cost, though perhaps there is more obvious scope in regard to this than as regards increasing the conductivity of conductors. In a recent speculative article of American origin by Dr. J. A. L. Waddell, I notice that the writer prophesies the discovery of an alloy of ten times the conductivity of copper, but, so far as we at present know, all alloys have a worse and not a better conductivity than their elementary constituents; and though, so far as I am aware, no special investigation has ever proved that this is a natural law that cannot be overcome, still conversely there are no data to show that improvement can be looked for in this direction. True, Dr. H. K. Onnes, of Leyden, has not long ago shown that, by reducing the temperature of metals to the temperature of liquid helium, or to within less than 4° of the absolute zero of temperature, or more than 450° below zero Fahrenheit, these lose practically all resistance, and become nearly perfect conductors. Under these conditions an electric current, once started by an electromotive force applied to a cooled mercury ring, was found to persist for hours after the electromotive force had been removed—truly a startling effect, and one calling to mind Ampère's theory of permanent magnetism, according to which the magnetism is supposed to be due to molecular electric currents that persist indefinitely. Still, even to those most anxious to do their best to believe in the wonders of the future, the cooling of electrical conductors by passing through them streams of liquid helium, in the case of the thousands of miles of such conductors that are requisite for electrical distribution, does not appear to be a very practicable proposition. However, results like those obtained by Onnes give one furiously to think, and there are other solutions that are possible though at present far from without our grasp. For instance, no one knows what improvement is yet to be obtained in the conductivity of metals by further purification, and especially by freeing them entirely from occluded gases. Electrolytic copper, which is specially pure, has already a conductivity measurably in excess of what was obtainable by the older methods of refining, while it has been found that in the case of palladium the extraction of the occluded hydrogen materially improves the conductivity. Possibly similar treatment might lead to important results with other metals. The subject is still largely unexplored, but if any such practical method could be devised for diminishing the resistance of conductors, it would be a most important matter, as the enormous amount of copper at present required for any very large and widespread scheme of electrical distribution presents a very real difficulty.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, November 22, 1918.

Prof. C. H. LEES, President, in the Chair.

A "Note on the Linguistic Nomenclature of Scientific Writers" was read by Mr. A. CAMPBELL.

The Note insists on the importance of clear and consistent nomenclature and the avoidance of foreign plural forms, such as *media*, *genera*, *radiivectores*, &c. The term *pulsance* is suggested as a suitable name for $2\pi \times$ frequency.

DISCUSSION.

Mr. A. P. TROTTER said that he often thought the valuable work done by Prof. S. P. Thompson, Mr. Duddell, and Dr. Russell in connection with the nomen-

clature of electrical engineering might have been taken up in connection with other sciences. The Americans were coining new scientific terms much too fast—in photometry, for instance—and many required careful definition and the restriction of their use to their proper spheres. The work on the Electrical Engineering Nomenclature Committee had been most interesting, and he thought a small committee of the Physical Society could profitably take the matter up.

Dr. A. RUSSELL congratulated Mr. Campbell on raising an interesting question. Personally he was indebted to Mr. Campbell for many words. As regards classical plurals, it was always rather unpleasant to him to hear words like memorandums, radiuses, &c. Lemma had been mentioned by Mr. Campbell; he always regarded this as being an English word as much as Greek, and thought in most cases it should be left to the literary sense of an author which form of plural to use. As regards ω , this he always looked on as the angular velocity of a rotating vector, and had never found it necessary to use a specific word for it.

Prof. G. W. O. HOWE pointed out that one could not correctly say "an alternating current with an angular velocity ω ," since the angular velocity had no reference to the physical alternating current, but only to its graphical representation; one could avoid the difficulty by saying that the current had a frequency $\omega/2\pi$. Some years previously, when he had been on the staff of a firm in Berlin, there was a strong feeling among a number of German engineers against the introduction of non-German technical words. The word *Telephon* was replaced by *Fernsprecher*, and objection was taken to such words as *booster*, the synthetic German compound word being insisted upon. As an indication of the interest taken in such questions, it may be mentioned that, by a mutual agreement among the members of the staff of one department of the works, anyone who at the luncheon table used a word which was not of pure German origin was fined for the benefit of a common fund.

Prof. A. W. BICKERTON said that he had found a serious deficiency in words when working out his new cosmic generalisation, and had found it convenient to coin several new terms. For instance, he had used the word *kinetol* to represent the kinetic energy of unit mass, and *thermatol* the amount of thermal energy per unit mass, &c.

Mr. C. C. PATERSON said that the termination *-ivity* to indicate a specific quality of a material was one that should be more widely employed. He thought the termination *-ance* should always be carefully limited in its application. It was dangerous to limit the meanings of all words too closely, as there are then no words left for general conceptions. The Americans have already used up nearly all the available terms, and earmarked them for particular meanings. Almost the only one not so treated is *light*.

Prof. LEES said that we appeared to delight in language irregularities. For instance, probably everyone was agreed on the pronunciation of the words *nation*, *national*, but what about the similar pair *ration*, *rational*?

Mr. T. SMITH (communicated remarks) considered that the note called attention to a matter which had been neglected to a most unfortunate extent. He must plead guilty to having regularly used some of the plurals to which the author took exception, the forms used being, so far as he had noticed, those most frequently employed. A liberal-minded committee charged with the duty of admitting and systematising new scientific words and encouraging their use would be of great assistance at the present time, but there would unfortunately be a considerable risk that a committee appointed for this end would contain a strong conservative element, which would perhaps tend to grow stronger as time went on whose object would be to strangle words struggling for recognition. An illustration of the unfortunate tendency in English to combine two words on one of which a large variety of meanings was thrust, rather than to coin short new words for funda-

mental ideas, could be drawn from optics. The word *power* was used by itself to denote a definite property of a lens; the same word was also used in *resolving power*, there being no connection between the *powers* in the two cases. Again, *magnifying power* was used of telescopes and microscopes with different meanings in the two cases. Many other illustrations could be given, but it was clear that the time had come when an attempt should be made to deal with the matter systematically.

Mr. CAMPBELL, in reply, said he had been much interested in the various comments. He would like to draw Mr. Trotter's attention to the work which a nomenclature committee of this Society had already done. Dr. Russell's remarks mainly amounted to saying that having done a thing habitually he did not like to change the habit. But very little practice gets over the repugnance. As regards Mr. Paterson's complaint about over-limitation, there were at present too many loosely used words in scientific terminology. For instance, *pressure* had been stolen from dynamics, and used to mean voltage or potential difference. If chemists were to use the same name for different things in this way there would be frequent cases of poisoning. He agreed with Prof. Howe's objection to calling $2\pi\nu$ an angular velocity. He was glad to hear Prof. Bickerton's remarks on the need of new terms in astrophysics.

The following three notes were then read by Mr. CAMPBELL:—

"A Note on Low frequency Microphone Hummers."

The note describes the conditions of mechanical loading, capacitance, and position which the author has found give successful working at low frequencies.

"A Simple Tuning Fork Generator for Sine-wave Alternating Currents."

The arrangement consists of an electrically maintained tuning fork, to one prong of which is attached to a small thin coil with its axis perpendicular to the direction of motion of the prong. As the fork vibrates the coil oscillates in the field of a fixed horseshoe magnet and an approximately sinusoidal E.M.F. is set up in the coil. The frequency with the apparatus shown was 10 vibrations per second.

"A Method of Comparing Tuning Forks of Low-frequency and of Determining their Damping Decrements."

The method consists in putting the windings of the maintaining magnets in series with each other and with a sensitive vibration galvanometer. The beats are clearly shown by the pulsations of the band of light on the scale.

DISCUSSION ON PREVIOUS THREE NOTES.

Mr. D. J. BLAICKLEY said that in connection with the harmonics or partial tones there was considerable confusion of terminology. Some writers confine the term *harmonics* to those in arithmetical progression with the fundamental. Partial tones not in this series should simply be called partial tones. For instance, in a tuning fork the first partial tone is not harmonic.

Dr. D. OWEN thought the vibration galvanometer method for comparing frequency and measuring decrements was much better than any method using a telephone. Why was the method principally applicable to low-frequency forks? With regard to the tuning fork generator, he could not see on what grounds Mr. Campbell states that he gets a sine-wave current.

Mr. I. WILLIAMS asked if Mr. Campbell had tried an electro-magnet with this apparatus. One could then control the shape of the field, and therefore the wave form of the E.M.F.

Mr. L. HOPWOOD said he would like to thank Mr. Campbell for the helpful remarks with which the demonstration had been accompanied. If he had had that information early in the war it would have saved him a considerable amount of wasted time.

Prof. LEES said he was interested in the point about the influence of the measuring apparatus on the results. He thought the effect would be very small. We know the

amount by which damping modifies frequency and the pumping due to the power taken by the galvanometer was very little. In connection with the position of microphones he had once been experimenting with a diaphragm. When tilted so that the concavity due to gravity was upwards, it worked regularly. In other positions it was much less regular.

Mr. CAMPBELL said he was interested in Mr. Blaickley's remarks. He was right as to the nomenclature of partial tones and harmonics. Even Lord Rayleigh, he thought, called the tone at 666 the first harmonic of the 100 fork. So did the French writers. In reply to Dr. Owen, he only mentioned low-frequencies because the method was the only one suitable for these frequencies. Higher frequencies could easily be done acoustically. With regard to the wave-form obtained with the generator, if one waves a bit of paper rapidly to and fro in front of the galvanometer shot it is clear that the E.M.F. is nearly of sine form. This was all he claimed for it at present. With regard to Prof. Lees' observations, he quite realised that the effect of the damping on the frequency of the forks would be very slight, but he was rather thinking of the effect of resonance in pulling the two forks more nearly together. The explanation of the behaviour of the telephone diaphragm mentioned by Prof. Lees might probably throw light on the behaviour of the hummers. He had never known why the tilt was effective.

Prof. BICKERTON—Why is not the horizontal position best, then?

Mr. CAMPBELL—Probably in that case the tighter packing of the granules interferes with the efficient working.

MISCELLANEOUS.

Employment of Demobilised Soldiers and Sailors.—No more urgent task follows upon the demobilisation of the forces than the re-instatement in civil life of the soldiers and sailors. The number of men to be dealt with in this country alone makes the labour gigantic; but the machinery exists for performing it, and it only remains for intending employers and employees to avail themselves of their opportunity. The Employment Exchanges, assisted by the Local Advisory Committees, which represent equally the interests of both parties in every neighbourhood, have the organisation ready for use. The staffs of the Exchanges have been considerably strengthened in order to meet the extra strain thrown upon them. It is not generally known that branches have been set up to deal with discharged men only, and in a great number of cases special sections for disabled men having been established. As far as possible, the work in these new additions to the Exchange system is carried on by men in the same position as those whom they are helping back to civil employment. Discharged men, with no small proportion of disabled among them, superintend the placing of discharged and disabled men. It has been found that the loss of an arm, of a leg, of two legs, and even of eyesight is no insurmountable obstacle to the performance of efficient work, giving employers who will employ the men, and the Exchanges which make use of such men are patent examples of the fact that war, even when it has dealt serious bodily injuries, does not unfit the fighter for successful life as a civilian.

Determination of the Molecular Complexity of Liquid Sulphur.—Alex. Mitchell Kellas.—The author has found that, contrary to the statements of various observers, the surface tension of liquid sulphur can be determined by means of capillary tubes between the melting-point (115°) and the boiling-point (445°). Impurities (especially sulphuric acid, sulphur dioxide, and hydrogen sulphide) must be previously removed. Sulphur can be purified by distillation and subsequent boiling in dry nitrogen, the gases evolved being pumped off. The mean value for five capillary tubes gave surface tensions

of 60.46 and 56.38 dynes respectively for 119.4° and 156°. The molecular complexity of at least 95 per cent of mobile sulphur (S_8) between 115° and 160° is presumably represented by the formula S_6 , assuming the validity of the Ramsay and Shield method of calculation. The surface tension of viscous sulphur falls continuously from the melting point to the boiling-point, being 48.2 dynes at 280 and 39.1 dynes at 445. The molecular complexity alters about 160°, and it might be stated as a first approximation that an endothermic termolecular polymerisation appears to occur near that temperature $3S_6 \rightleftharpoons (S_6)_3$. The aggregate S_{18} seems to be stable up to near the boiling-point. The polymerisation may be due to a tendency of sulphur to lower its valency with rise of temperature, the complex S_6 possessing a residual valency at 160°. Other methods of calculation of molecular complexity seem to emphasise the aggregate S_6 , but the results do not seem to accord with experimental averages as well as those of Ramsay and Shield's method.—*Journal of the Chemical Society*, No. 674, p. 903.

Electrolytic Disinfectant in Influenza.—In view of the Memorandum on Epidemic Influenza which has been issued by the Royal College of Physicians of London (*The Lancet*, Nov. 16, 1918), in which, as a preventive, is recommended gargling the throat with 20 drops of solution of chlorinated soda in a tumbler of warm water and sniffling up the nose a solution of common salt, Mr. F. W. Alexander, medical officer of health of Poplar, sends us an account of the method adopted in that borough for dealing with the outbreak. The drawbacks to using chlorinated soda on a large scale are that it is difficult to make and has to be freshly prepared. The electrolytic fluid as made in Poplar contains common salt and hypochlorite of magnesium (a solution of chlorinated magnesium), it is alkaline and stable, and if it is necessary to give it a tint permanganate of potash may be used for the purpose, as it retains its colour when added to the solution. During the first three weeks of November 5370 gallons were distributed free in the borough, the cost, including that of electricity and materials, being 3d. per gallon (or about £12 per 5370 gallons). This fluid has been available free in Poplar for the last twelve years, and as soon as influenza broke out in the borough handbills were distributed and the district posted with bills instructing the inhabitants to rinse the mouth, gargle the throat, and douche the inside of the nose with the council's electrolytic disinfectant, which could be procured free at one of the council's seven distributing depôts. Mr. Alexander points out the advantages of installing plants for making the fluid, especially on ships and at seaside towns, where the electrolyte is always at hand and always ready. It could be used immediately in outbreaks of diphtheria and cerebro-spinal fever.—*The Lancet*, January 11, 1919.

MEETINGS FOR THE WEEK.

TUESDAY, 25th.—Royal Institution, 3. "Lessons of the War," by Prof. Spenser Wilkinson.

WEDNESDAY, 27th.—Royal Society of Arts, 4.30. "Food Production by Intensive Cultivation," by F. Keeble, C.B.E.

THURSDAY, 30th.—Royal Institution, 3. "Chemical Studies of Oriental Porcelain," by Prof. J. Norman Collie.

— Royal Society "Investigation of extreme Ultra-violet Spectra with a Vacuum Grating Spectrograph," by J. C. McLennan and R. J. Lang. "On the Absorption Spectra and the Ionisation Potentials of Calcium, Strontium, and Barium," by J. C. McLennan and J. F. T. Young. "Vacuum Arc Spectra of various Elements in the Extreme Ultra-violet," by J. C. McLennan, D. S. Ainslie, and D. S. Fuller. "Emission and Absorption in the Infra-red Spectra of Mercury, Zinc, and Cadmium," by R. C. Dearn. "Measurement of Magnetic Susceptibilities of Low Order," by E. Wilson. "Experimental Determination of the Ionisation Potential for Electrons in Helium," by F. Horton and Ann C. Davies.

FRIDAY, 31st.—Royal Institution, 5.30. "Giant Stars," by Prof. H. H. Turner.

SATURDAY, Feb. 1st.—Royal Institution, 3. "The Works of J. S. Bach," by Prof. H. P. Allen.

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THE CHEMICAL NEWS

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THE MOTOR FUEL PROBLEM

By W. R. ORMANDY, D.Sc.

THE author proposes to give in this paper a *résumé* of some of the more important aspects of a very important subject, rather than to bring forward original ideas.

The motor industry may be classed as one of the greatest in the world, and yet little systematic investigation has been made with regard to the foundation on which it has grown up. A conservative estimate of the annual wages paid in the manufacture of motor bicycles, motor-cars, and heavy vehicles such as motor buses and lorries would be £10,000,000, without taking into account the dependent industries devoted to the manufacture of all classes of accessories. The wages bill of the latter, and the wages paid for the repair, upkeep, and accommodation of the large number of vehicles in use, are practically impossible to estimate. The industry has attained such magnitude in the United States of America that a motor vehicle has come to be looked on rather as a necessity than a luxury. There is no doubt that the demand for motor fuel will increase to an enormous extent after the War, not only for the types of vehicles mentioned above, but also for motor-propelled boats, agricultural appliances, and aeroplanes. The normal demand for motor-spirit in this country alone would now amount to some 200,000,000 gallons per annum, and this country is not exceptional.

The best known fuels at present in use are the petroleum products, and practically the only source of supply of petrol in the early days of the industry was the United States. Other oilfields were, however, developed as the demand grew and the output of our important American field fell off, and suppliers were enabled to meet the increased demand, largely by the employment of cracking processes and the recovery of spirit from natural gas. It is probable, however, that, although the supply may be sufficient to meet the demand for some years to come, the rapidly increasing demand will render necessary the adoption of substitutes for petrol at no very distant date.

Fuel may be conveniently divided into three physical groups, viz., solid, liquid, and gaseous.

Of the former class, coal, coke, and charcoal are the most important to be considered. Coal may be employed in two ways, either in a suction or other gas producer plant, the gas being used to drive an internal combustion engine, or as a fuel for steam raising. The former alternative presents many difficulties, more especially when a bituminous coal is considered, the most serious of which is perhaps the difficulty of washing the gas. It is, however, possible that such a system may find an application in the heavier vehicles. The prospects of steam-driven motors are somewhat more favourable, although it is hardly likely that, even in heavy vehicles, the steam-engine and boiler will become a serious competitor of the internal-combustion engine.

Much attention has recently been devoted to the use of coke as a fuel in the Clarkson motor-bus, which formerly ran on paraffin, until the high price and scarcity of the latter fuel became serious. Wood charcoal appears to have little future, owing to its bulk and high price, but there appear to be distinct possibilities of the use of charcoal produced from woody lignites found in Ireland.

It is well known that ordinary town gas can be successfully used in high-speed motors, about 250 cubic feet of

normal gas being equivalent to a gallon of petrol. This knowledge has led to the extensive use of coal gas for testing engines, and also to its use on the road, but the development of the latter calls for the design of a suitable container to carry gas under high pressure. Valuable investigation work in this direction has been undertaken by the Government, a Committee having been appointed under the chairmanship of Sir Boverton Redwood.

Turning now to the liquid fuels, the paraffin series can be divided into three classes—first, the more volatile products of distillation classed broadly as petrol; second, what is generally known as paraffin; and, third, solar or fuel oil, used in the Diesel and semi-Diesel engine, and as fuel for steam raising. Of these three classes the first is undoubtedly the most important, including as it does benzol, a coal-tar distillate which gives excellent results in a petrol engine with very slight alteration of the latter. The earlier forms of bee-bive coke-ovens for the production of coke have been largely superseded by by-product recovery ovens, which are equipped with the necessary plant for the recovery of the volatile by-products, amounting to from 1½ to 3½ gallons per ton of coal carbonised.

The fractionation of coal-tar produced in gas-works yields a small quantity of volatile liquids and a larger proportion of oils. Recovery plants have now been installed at most of the large gas-works for the recovery of benzol and toluol, from one to two gallons of these liquids being obtainable per ton of coal carbonised. It is probable that some 50,000,000 gallons of volatile liquid coal-tar distillates per annum will be available after the War.

By the distillation of bituminous shales, of which immense beds are to be found in Great Britain, a series of liquid products can be obtained ranging from a volatile spirit to a heavy lubricating oil. This industry is at present little developed, except near Glasgow. These shales yield also sulphate of ammonia, which is of value as a fertiliser, and the shales found in England contain a considerable percentage of deleterious sulphur compounds, which render purification processes necessary. It will be necessary to devote much attention to the distillation industries in the future.

A liquid which merits serious consideration as a petrol substitute is alcohol. Although its calorific value is lower than that of benzol and petrol, and it is not so readily inflammable, the fact that it can be produced cheaply and in large quantities make it a serious competitor as a fuel for internal combustion engines. It can be produced from materials containing starch, sugar, or cellulose, but at the present time it would hardly be possible to consider its production from sugar- and starch-producing materials, as these are nearly all required for foodstuffs. With the present agricultural outlook in England, however, with prospects of growing more cereals, greater quantities of root crops must be produced, and the result will be over-production of turnips and mangolds, unless land is put under beet, which indeed is a better cleaning crop than mangolds or turnips. As heavy a yield of sugar-beet can be obtained in this country as on the Continent with a sugar-content as high or even higher. By adopting this expedient, a portion of the internal demand for sugar could be met, and the residue of the beet would be available for the manufacture of industrial alcohol. At the same time sugar-cane residue could be utilised at various centres abroad to supplement the home production. Hitherto alcohol has been produced industrially from potato-starch in Germany, from sugar products in France, and from maize in America; but in this country the Government has not encouraged the production. The preparation of alcohol from potatoes was not adopted in Germany on account of cheapness, but in order to encourage agriculture. Imported molasses or maize and many other products would be cheaper, but the adoption of one or other of these would not have enabled a large population to live on the land. The average price obtained for alcohol potatoes was only about 22s. per

* Abstract of Paper read before the Institution of Petroleum Technologists, November 19, 1918.

ton, but after distillation the residue was available for cattle, and the operation of the distilleries afforded employment during the winter. The yield of 95 per cent alcohol would be about 20 to 25 gallons per ton of potatoes, but a much higher yield, of the order of 75 gallons per ton, may be obtained from grain, owing to the higher percentage of starch, and alcohol could be produced in some of our colonies at a price of about 3½d. per gallon for raw material.

Much attention has been devoted to the production of alcohol from cellulose in America, an output of 30 to 40 gallons per ton of wood treated being obtained. The initial difficulties have to a large extent been overcome, but there is still room for much experimental work.

Sulphite wood-pulp residues have been used to a large extent in Norway and Sweden, and it is expected that both of these countries will become independent of foreign supplies of motor fuel. This process would be of little interest in England, but there are great possibilities in it for some of our colonies. The same remarks apply to the synthetic preparation of alcohol, which depends on the availability of ethylene and acetylene, for the production of which chemicals cheap electric energy is essential.

Many plants consuming alcohol existed on the Continent before the War, and experience with them goes to show that a higher thermal efficiency can be obtained than with petrol, and that no special corrosion takes place, contrary to what has been so often urged as an objection. For use with engines designed to run on petrol alcohol alone would not be suitable, but a mixture of two parts of alcohol to one of benzol gives good results, provided that suitable means are adopted for heating the air supplied to the carburettor, and that a somewhat larger jet is used. The present supply of benzol, with a proportional amount of alcohol would therefore go far towards meeting the present demand for fuel, and could always be supplemented by the production of an ethyl ether from the alcohol itself. Further, the supply of benzol could be considerably increased by paying attention to the distillation of low grade coals, but the practicability of installing recovery plants naturally depends on the price commanded by the motor fuel. There is no doubt that the question of cheap power will be of enormous importance in the future, and that the provision of cheap power is largely dependent on the utilisation of cheap and hitherto wasted materials. Gas works would be more ready to devote attention to the recovery of benzol if gas for private consumption were sold on the basis of calorific, rather than lighting, value.

The increased demand for petrol of late years has led to the supply of a liquid of higher boiling point and higher specific gravity, but a certain proportion of constituents of lower boiling-point is necessary in a motor to facilitate starting. Benzol is a suitable constituent for such a mixture, and its use would enable petrols of even higher boiling-point to be employed. The price of petrol has hitherto been the highest that the public will pay, but the question of a cheap and reliable fuel is one of national importance. It is important therefore that the output of benzol should not get into the hands of petroleum companies, as, if it did, they would have an obvious interest in opposing the preparation of alcohol on a large scale. The motor fuel problem should be faced and solved at once by united action on the part of motor-builders and users, and revision of the present Excise laws should be secured.

The use of a new fuel brings in its train new problems in lubrication. Trouble has been experienced in bearings when a mixture of paraffin and petrol has been employed as fuel, probably owing to the reduction of the viscosity of the lubricating oil by the admixture of a quantity of the paraffin with it. There is great need of research work, not only in this connection, but also with regard to the best limits within which alcohol-benzol mixtures can be employed and the viscosity of various mixtures.

Further problems arise in connection with the amount of water which can be contained in an alcohol-benzol mixture, and the possibility of adding paraffin compounds, and the rate of flame propagation in alcohol-air mixtures.

The problem of the development of alcohol as a fuel has received much attention in recent years, and a number of Committees have been formed, but although they have been unanimous in deciding that alcohol is the only suitable alternative fuel in view, there has been no practical outcome of their deliberations. An Inter-Departmental Government Committee is now in existence to deal with the subject of alcohol in its aspect as a motor fuel, and it is to be hoped that with the full support of the motor industry it may achieve useful results.

ON THE OXIDATION OF COAL.

By J. R. PARTINGTON, D.Sc.

IN an interesting recent paper on the subject of the oxidation of coal at low temperatures, Dr. R. V. Wneeler (*Trans. Chem. Soc.*, 1918, cxiii.-cxiv., 945) has explained some valuable experimental results by a hypothesis which he states as follows:—"The first step in the oxidation of coal is the formation of an addition compound, or complex, of oxygen with one or more of the substances present in coal."

It is suggested that this hypothesis, which is of itself not very probable, does not account for the observed results, and that it should be replaced by another hypothesis, which it is the purpose of this note to explain.

A mixture of gases is brought in contact with freshly hewn coal deprived of its occluded gas, adsorption takes place on the surface of the coal. If moisture is present in the gases it will be adsorbed in larger quantities than the permanent gases, so that the permanent gas adsorption with dry air should be greater than with moist air. The adsorbed layer of gas, being under high pressure, will react, more or less rapidly, with the coal, and oxides of carbon will be produced. If the adsorbed gases are pumped off there will therefore be found in them oxides of carbon in amounts depending on the time the adsorbed gas has remained in contact with the carbon, and residual atmospheric gases. If the air was initially moist, the amount of permanent gas will be much less, because of the preferential adsorption of moisture, which occupies the adsorbing surface with greater tenacity, to the almost complete exclusion of permanent gas, which is adsorbed with much less tenacity.

Further, if the process whereby atmospheric gases are taken up by coal is one of adsorption, the pressure of the air brought in contact with the coal will at first fall very rapidly for a short period, and will then gradually fall off until adsorption equilibrium is reached. If the adsorbed layer penetrates into the bulk of the adsorbent the very slow final fall of pressure may go on for a very long time, as has been shown by the experiments of McBain.

The adsorbed layer will then begin to react, possibly slowly, with the production of oxides of carbon. There is every reason to believe that the primary product of the interaction of carbon with oxygen is carbon monoxide alone, as has been maintained by Dixon. The reasons for this conclusion may be briefly summarised as follows:—

1. When perfectly dry carbon burns in perfectly dry oxygen (*i.e.*, the substances dried over phosphoric oxide) carbon monoxide is almost the sole product (Baker).
2. When the diamond burns in a current of oxygen a flame of burning carbon monoxide appears (Macquer).
3. When a thin bed of incandescent coke is blasted with air large quantities of carbon monoxide are produced (daily experience).

There is reason to believe that when carbon dioxide is produced it is always produced as a result of an interaction with water, the latter acting as a catalyst in the manner described by Dixon: $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$.

The carbon dioxide produced in the oxidation of coal is therefore probably derived in this way, or else by the direct interaction of adsorbed moisture with carbon: $\text{C} + 2\text{H}_2\text{O} = \text{CO}_2 + 2\text{H}_2$.

The hydrogen produced may be wholly reoxidised, or retained on the absorbent, or traces may escape. Dr. Wheeler does not appear to have looked for hydrogen in his gases, although this is a most important point.

Let us now see how this hypothesis explains the results obtained by Dr. Wheeler. We may conveniently give these in the form used in his paper, as it will then be obvious how many more important results, on which he lays little or no emphasis, are completely in accordance with the new hypothesis.

1. "The absorption of oxygen" [nothing is said of the nitrogen and moisture which are equally important] "by newly won bituminous coal is initially very rapid, even at ordinary atmospheric temperature, but this rapid absorption soon gives place to a slow but long-continued absorption."

These results are exactly what one would expect if the phenomenon were one of adsorption; the adsorption would occur more readily at lower temperatures (a fact overlooked by Dr. Wheeler, who speaks of "even at ordinary atmospheric temperature"). If the reaction were one of combination, with formation of a complex oxide of carbon, we should, on the contrary, get an absorption until the dissociation pressure of the oxide was reached, when the pressure would remain constant. If gas is now pumped off, the pressure should remain constant and equal to the dissociating pressure of the oxide, until the latter is completely decomposed, when the pressure should fall rapidly to zero. I do not know if Dr. Wheeler has ever noticed the latter effect; it is a necessary consequence of his hypothesis.

2. "The initial rapid adsorption of oxygen at low temperatures is not accompanied, as far as could be ascertained, by the formation of water or oxides of carbon, but during the second slow phase of the absorption these products of oxidation make their appearance, the amounts increasing with the temperature of the coal."

These results are equally well explained on either hypothesis; the appearance of the products during the second phase is due to their displacement from the adsorbed layer by the unaltered atmospheric gases, which then begin to have an influence on the adsorption equilibrium.

3. "The ratio, CO_2/CO , in the products of combustion remained appreciably constant for a given coal at a given temperature throughout the long-continued slow adsorption of oxygen, the ratio decreasing with increased temperature."

This result is at once explained if the oxidation occurs through the intermediary of moisture, since the ratio CO_2/CO in the water-gas equilibrium is decreased by an increase of temperature. It may be that the ratios found by Dr. Wheeler are the equilibrium ratios for that reaction at 100° ; they may equally well not be, on account of the modification of the equilibrium by surface forces. Dr. Wheeler's own hypothesis appears to offer no explanation of this result.

4. There is an additional new fact which Dr. Wheeler refers to as follows:—"A more important observation is the marked increase in the quantity of gas retained by the coal when the air passed over it was dried by calcium chloride." He does not attempt to explain this, dismissing it as "a matter requiring further study," although it appears to offer the key to the correct interpretation of the whole phenomenon. The result follows at once from the hypothesis of adsorption; we should expect the quantity of nitrogen to be largely increased with dry air, whilst the quantities of CO_2 and CO should be decreased; further,

since the formation of CO_2 is the result of a secondary reaction involving moisture, whilst that of CO is a primary reaction, we should expect the ratio CO_2/CO to fall when the moisture is removed to the stage possible with calcium chloride. All these results, which are entirely inexplicable on Dr. Wheeler's hypothesis, follow at once from the adsorption hypothesis, and that they are the observed results is seen from the following table taken from that author's paper:—

Treatment	Vol. of gas removed between 15° and 100° .	CO_2 .	O_2 .	CO .	N_2 .	Ratio CO_2/CO .
A. Moist air at 15°	17.7	28.0	2.8	2.2	67.0	12.7
B. Dried air at 15°	30.8	15.4	Nil	1.8	82.8	8.6
C. Moist air at 50°	18.7	42.0	4.7	3.9	49.4	10.8
D. Dried air at 50°	27.0	12.8	1.5	1.7	84.0	7.5
E. Moist air at 100°	6.8	77.0	1.8	13.2	8.0	5.8
F. Dried air at 100°	8.9	31.3	0.2	8.3	60.2	3.8

The fall of the ratio CO_2/CO with rise of temperature is well marked, as is the increased ratio of N_2 to oxides of carbon in the case of dried air.

It is seen that the new hypothesis is capable of explaining all the facts explained by Dr. Wheeler's hypothesis; that it is capable of explaining all the remaining facts which are not explained by the other hypothesis, and that it is in complete accordance with all that is known of the adsorption of gases by solids. It introduces no new assumptions, whereas Dr. Wheeler has to put forward the assumption of a purely hypothetical chemical compound, the behaviour of which is not amenable to numerical calculation, and the existence of which is highly problematical.

SCIENCE AND THE FUTURE.*

By ALAN A. CAMPBELL SWINTON,
F.R.S., M.Inst.C.E., M.I.E.E., M.I.Mech.E.

(Concluded from p. 46).

It would also be rash to deny too absolutely the possibility of the wireless transmission of electric energy in bulk. The fact that enormous quantities of energy come to us in this way from the sun, with a transmission density that near the sun's surface is immense, shows what the ether is capable of doing. The production of plane waves would help the solution of the problem, but there is the difficulty of so concentrating and directing the waves that they may all be received on a limited area. Perhaps, however, it may be found that though electro-magnetic waves cannot be driven to go exactly and only where is wished, they can possibly be led there. It is a problem at present beyond our ken, but so many marvels come to pass that one can never be sure of what may be brought about, provided always that no natural law stands in the way.

The economical generation of electricity from coal is however not merely a question of the scale upon which the operation is conducted, important up to a point though that condition is. In addition to its heat or energy giving properties, coal contains a number of constituents of great value, such as the tar from which the aniline and other dyes, and many other chemical products most useful in medicine, photography, and in the arts, are derived, together with tolual for explosives, benzene and other derivatives, including sulphate of ammonia, which is in great request as an agricultural fertiliser. Where the coal is simply burnt in a furnace, as in ordinary steam-boiler practice, all these are lost; but when it is first turned into gas these most valuable by-products, which are nowadays

* An Address delivered at the opening meeting of the 165th Session of the Royal Society of Arts on November 20, 1918. From the *Journal of the Royal Society of Arts*.

the chief stand-by of the gas industry; can be saved and turned to account. Up to now it has not been found economical to apply this refinement to electrical generating stations except in rare instances, but with larger stations and ample capital, and more especially with coal at increased prices, it is to be hoped that something in this direction may be found practicable on an economic basis, while it is even possible that it may be found necessary for the State to declare such preservation of the by-products imperative and make it compulsory. Furthermore, in electrical generation there is the very important matter of what engineers call the load factor, by which is meant the ratio of the actual amount of electric energy that a generating station supplies, to the amount that it could supply were it always working at full power. Lighting, and even ordinary motive power requirements, only last for a few hours in every twenty-four, so that while generating machinery has to be provided, sufficient to deal with the maximum load at any one moment, in many cases a large proportion of the machinery is not required, and has to stand idle for a considerable portion of each day. As interest on the capital that machinery represents is mounting up all the time, and as there are many costs of labour, and of fuel, which are not diminished in proportion as the load becomes a minimum, this is obviously very uneconomical. This is particularly so because with electricity, unlike gas, storage on any large scale is too costly to be practicable. It is thus most important, in order that electricity should be generated cheaply, that the gaps in the load should be filled up and the latter brought up as far as possible to a uniform maximum. With small stations, supplying limited areas, this is a difficult not impossible to attain, but where the supply is on a large scale, and distributed over a wide area, the diversity of uses at different hours of the day tends to equalisation, and assists the production of a load that corresponds more nearly to a steady one throughout the twenty-four hours and during every day of the year. This is the explanation of what many people fail to realise the reason for, namely, the difference in prices that the consumer has to pay for electricity for lighting, which, as stated, has usually only a short hour demand, and for heating and motive power purposes, where the hours of consumption are usually much longer. It is also to be hoped that the establishment of electro-chemical industries which take a continuous steady load, or better still can arrange to take energy only only at such times as it is not required for other purposes, will assist in regulating the consumption so that generation can be carried on continuously at a maximum rate with a minimum of cost. These considerations are, of course, a commonplace to all electrical engineers, but they are not perhaps understood as well as they should be by the public.

By far the most important requirement of mankind is energy in its various forms. Like all other animals, man could not continue to exist without a constant supply of the energy which is requisite for the internal processes of his body, for the work that he does with his muscles, and for the activities of his brain. It may be potential energy in the form of food, or kinetic energy such as he derives directly by conduction and radiation from his surroundings. Like the steam engine he must be stoked with fuel in order that he may develop mechanical power; and in order that he may exercise mental effort, like Babbage's calculating machine, he must be supplied with the equivalent of the energy required to turn the handle of that ingenious apparatus.

Nearly all our energy comes to us directly from the sun, though some portion is derived from the internal heat of the earth, and from terrestrial and lunar rotations. Moreover, what we get from the sun is transmitted to us from across the nearly ninety five millions of miles of intervening space by waves in the universal ether exactly analogous to those we use for wireless telegraphy. Some of this sun energy goes to warm the earth and its atmosphere and our bodies, some is radiated away again into space,

and some very small portion is stored in such a way that we are able to make use of it as we want it. The sun, whose temperature is about 6000° Centigrade, is constantly sending out some 9000 horse-power per square foot of its superficial surface, and as the diameter of the sun is about 865,000 miles, there are a great many square feet, so that the amount of energy the sun radiates is prodigious. As the energy is sent out more or less equally in all directions, only a very small proportion of the whole is intercepted by the earth, but even so there is no lack in the supply that the earth receives, which amounts in total to some 200 billion horse-power, or on the average to some 4,000,000 horse-power per square mile of that portion of the earth's surface that is exposed not too obliquely to the sun's rays. All our water power, except any that may be obtained from the tides, and what small amount of power we can get from the wind, are of course purely solar in their origin, being due to the results of evaporation and of the thermal dilation of the air. But apart from the direct heat we get daily from the sun, our main source of energy is of course coal, which has been called bottled sunshine, and consists of vegetable growth in which is stored energy received from the sun during millions of years, millions of years ago. Energy from the sun is still being stored in all plant life, but according to Nernst only to the extent of about three millionths of the total that reaches the earth. Moreover it is by no means an efficient process, most of the energy that falls on the leaves being absorbed in evaporation or otherwise lost, and the actual amount of energy stored, as measured by Dr. Horace Brown, is less than 2 per cent of that which reaches the vegetation. For our food this will no doubt suffice for many a millennium, especially with the intensive culture that Science can provide, but when we come to consider fuel for warming our bodies, for driving our machinery, and for industrial purposes generally, we must bear in mind that the amount of coal in the world is strictly limited. Many estimates have been made of its duration, but not only are data as to the amounts existing and available uncertain, but it is also difficult to foretell the rate at which consumption will increase. Anyway it runs into five or six hundred years for this country, and perhaps nearly ten times as long for the whole earth. Sooner or later, however, it will all be used up, and mankind will have to depend, no longer upon the stored energy of bygone aeons, but on the sun's actual daily supply. Economy in the consumption of coal is therefore a matter of great importance, especially in this country, where so much depends upon its use, and it is with this view that the present proposed large schemes for the economical generation and distribution of electric power have been put forward. Unfortunately nothing better than the heat engine, which includes all those engines that are operated by steam, gas, and oil, bounded as its efficiency is by the laws of thermodynamics, has hitherto been discovered to turn our coal and oil into mechanical work. Other methods which are not so bounded, and in which, instead of a maximum of perhaps 30 per cent, nearly a cent per cent transformation could possibly be obtained, are theoretically conceivable, but do not materialise. Methods on the principle of Grove's gas battery, which gives electric energy directly from the oxidation of hydrogen, and others in which solid carbon is used as the oxidised element in a primary electric battery, were at one time considered hopeful, but have accomplished nothing; while some years ago considerable stir was made by a primary battery, invented by Dr. Borchers, of Aachen, which was supposed to derive its energy from the oxidation of carbonic oxide to carbonic acid, but which, like some other German projects, proved unsound both in theory and in practice. Then there are quite other methods of converting heat into work, as, for instance, our old friend the thermopile. This has, of course, proved up to now a most ineffective appliance, and some years ago Lord Rayleigh showed that with the materials then used, but only in the special case of their use, it was of necessity inefficient. Has anyone, however, of late

years investigated the thermo-electric properties of all the new metals that the electric furnace, and other novel metallurgical processes, have recently provided, and of the alloys that these will make, and does anyone know how thermo-junctions, made of these or of the older materials, whose properties we are acquainted with at ordinary temperatures, would behave at temperatures so low that, as we have seen from the work of Onnes, all electrical resistance virtually disappears? All that can be said is that here are problems for the physicist and chemist which have great possibilities, if only they are investigated and solved whilst there is still plenty of coal left to be utilised. Seeing that the steam engine itself is not much more than a century old, and most of our electric knowledge is much younger, we need not perhaps despair even of this.

The importance of utilising the water power on the earth as a means of saving the consumption of coal is now thoroughly recognised, and is receiving the attention of the Governments of this and other countries. The amount, though large if everything available were utilised, is, however, insufficient to take the place of coal, while much of it exists in places remote from industries and population. This is without taking into account the power of the tides, which is enormous, but, it would appear, impossible to turn to practical use, in most places on any large scale, except at a cost which is altogether prohibitive. There is also the internal heat of the earth, which is actually at present being utilised near Volterra in Italy, where volcanic steam issuing from the ground is being successfully applied to work two 5000 horse-power turbines. This is a method which may perhaps be capable of considerable extension in various suitable parts of the earth, where volcanic forces come up to the surface, and are not too destructively active, but even so, the total amount of energy likely to be obtained in this way is comparatively insignificant. There is also the question whether, if, as some suppose, mineral oils are produced in the bowels of the earth by the action of super-heated steam on the carboniferous rocks, this process is still going on at any useful rate so as to maintain the supply. Any evidence that there is appears, however, to be against this supposition, for all the older oil-fields of the United States already show signs of becoming exhausted, while it is by no means certain that oil, like coal, is not a product of solar radiation stored over vast periods of time, and, anyway, the quantity of oil that appears to be obtainable is only a very small amount compared with coal.

When therefore the coal is exhausted it would seem that in the main recourse will have to be had to the enormous flood of solar radiant energy that is continually falling on the earth, and the problem is how this can best be utilised. The most obvious method is of course to grow plants, stimulating them in every way that Science can devise, and cultivating especially those which grow most rapidly and are specially suitable for the production of fuel. Such fuel need not, however, take the crude form of mere fire-wood, but more likely it will be best to cultivate plants that store the solar energy in the form of starch and sugar which can be converted into alcohol, as is already being done on some scale in order to supplement petrol for motive purposes.

As, however, vegetation is, as we have seen, an exceedingly inefficient accumulator for the storage of solar energy, and as there is the further inefficiency of the heat engine to be taken into account before mechanical power can be realised, there arises the question whether Science cannot devise some other and more efficient method of converting solar radiation into work, leaving altogether on one side the organic world and the means that plant life affords. Solar engines, in which the heat of the sun's concentrated rays in tropical climates is employed to boil water or other more volatile liquids, and thus operate steam engines, are by no means new, but owing to their considerable first cost per horse-power, and their great cost of upkeep, have never been so far proved commercially practicable, even where coal is exceedingly dear. They also suffer in

an extreme degree from the limitations of all heat engines, inasmuch as they cannot take proper advantage of the extremely high temperature of the sun, but have to work at a much lower temperature, which implies degradation of the energy and loss. But happily solar heat engines do not exhaust the possibilities of the case, as there remain other methods which, though still in the womb of the future as regards being worked out, can yet be indicated, and with regard to the success of which there is no inherent improbability. Photo-chemistry is usually associated with the art of photography, but really embraces a much wider field, the potentialities of which have as yet been but very imperfectly explored. The direct transformation of radiant energy into chemical, or even into electrical energy, is by no means impossible—indeed, as we have seen, the former transformation is already effected, inefficiently it is true, by plants; while it also takes place on a small scale in all photographic processes where light causes chemical reduction. Becquerel, in France, showed some fifty years ago how radiant energy could be transformed into electrical energy, and Minchin, in England, and others have also done the same by different methods. There do not appear to be any theoretical objections to success, nor to much higher efficiencies being obtained in this way than by organic means. No doubt the laws of thermo-dynamics apply to all photo-chemical action, but as the temperature of solar radiation is so very great this is of no large importance. Here then in photo-chemistry, perhaps in photo-electric chemistry, we have probably the most important problem that the Science of the future has got to solve.

Of late, in the world war, on many a stricken field, our own and our Allied Armies have been overcoming our adversaries and subjugating the powers of evil. In the future may we hope for conquest in even a wider realm. From now, let us look forward to the further triumph of Science over the forces of Nature, and to the bringing of these forces still more into subjection, for the common service of mankind, for—

"Peace hath her victories
No less renowned than war."

THE CONFIGURATIONS OF ORGANIC COMPOUNDS AND THEIR RELATION TO CHEMICAL AND PHYSICAL PROPERTIES.*

By ARTHUR MICHAEL.

(Continued from p. 43).

Substitution.—With unsaturation of contiguous carbon atoms, one of which is directly joined to a non-metallic atom, part of the bound energy thus liberated passes over into bound energy between the Δ -carbon and the negative atom, which causes a large increase in the hindrance to its direct replacement, and at the same time a great increment of free energy appears at the Δ -carbons. For these reasons a chemical change involving the non-metal in such substances, possibly with a few exceptions, passes over from a substitution process to that of a preliminary elimination or an addition (Michael, *Journ. Prakt. Chem.*, 1888, [2], xxxvii., 473; 1899, lx., 435; 1900, lxi., 448, Rule 11.).

The further behaviour of the primary reaction product depends on the chemical nature of the above-mentioned negative component on the hindrance to the separation of hydrogen from an adjacent carbon, and on the additive capacity of possibly reformed Δ -carbons for the reagent used.

Although stereo-structural and structural chemical changes are closely allied in this field a comprehensive discussion of these complicated relations will be reserved for a later paper (51), and the application of the underlying principles will be shown by analysing several reactions involving stereomeric changes.

* From the *Journal of the American Chemical Society*, xl., No. 11.

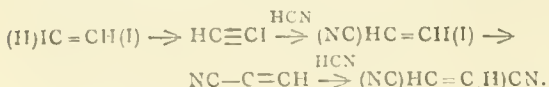
It should be premised that stereo-structural like structural chemical reactions tend to form new systems involving the maximum possible entropy change; i.e., the greatest possible conversion of the free energy into bound chemical energy and heat, and that chemical like mechanical force starts in the direction of the least hindrance to the change (*Journ. Prakt. Chem.*, 1899, [2], lx., 293; *Journ. Am. Chem. Soc.*, 1910, xxxii., 990).

Tanatar found that $\text{CH}_2=\text{CBrCOOH}$ (*Ber.*, 1880, xiii., 159), heated with alcoholic KNC and subsequent saponification, yields the maleate, a statement which has been doubted (Meyer-Jacobson, *Lehrb. Org. Chem.*, 1901, i., 412), as the current superficial views on this subject indicate the formation of a salt of $\text{CH}_2=\text{C}(\text{COOH})_2$.

The first phase in this reaction is the formation of a bromoacrylate with liberation of HCN, and as this substance shows a great additive power in a nascent state it and not the cyanide unites with the Δ -carbon atoms. In this addition the negative CN radical must go to the β -carbon, not only for its free energy is relatively positive to that in the α -carbon, but in so doing after the addition a more complete intramolecular neutralisation of the atomic energy is realised. Furthermore, this course of the reaction is favoured more by the behaviour of $\text{NC}-\text{CH}_2-\text{CHBr}-\text{COOK}$ towards the somewhat basic KNC than by that of the other possible compound; i.e., $\text{CH}_3-\text{CBr}(\text{CN})-\text{COOK}$. In the first product the affinity of H to C in CH_2 is greatly decreased by the negative CN, and the elimination of HBr proceeds with a slight expenditure of chemical energy (*Journ. Prakt. Chem.*, 1899, [2], lx., 292, Rule VIII.; and 1899, 361): in the other compound such a course of the reaction would proceed with such difficulty that the further change would consist in the direct replacement of Br by CN. The first product as a saturated derivative (*Journ. Am. Chem. Soc.*, 1918, xl., 707) should assume the configuration representing the maximum capacity to neutralise the alkali, which is when CN is in the cis-position to $-\text{COOK}$; i.e., $(\text{NC})-\text{CH}_2-\text{CHBr}-(\text{COOK})$, and which, through loss of HBr and saponification, should give the maleate.

The affinity of iodine for carbon and hydrogen is far less than that of bromine, and the value is so small in the alkylene iodides that they decompose easily with liberation of the halogen. With a compound like acetylene iodide there is a possibility of direct halogen replacement; indeed, the solid modification by heating with alcoholic KNC and saponifying the product thus formed has been converted into a fumarate (Keiser, *Am. Chem. Journ.*, 1890, xii., 99).

It would be a mistake to conclude definitely from this synthesis that the change proceeds by direct substitution. The primary action of the somewhat basic KNC may consist first in splitting off HI, and the next in the union of the iodo-acetylene thus formed with the nascent HCN; a repetition of these processes would lead, with trans-eliminations and trans-additions, to fumaric nitrile:—



According to this interpretation the maleinoid acetylene iodide would likewise pass over primarily into iodo-acetylene, and in that case it would also yield the fumaroid nitrile.

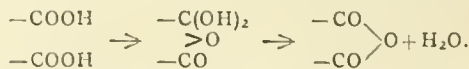
That certain stereomeric halogen derivatives give, apparently by substitution, the same reaction product may be explained in an analogous manner (Friedrich, *Ann.*, 1883, ccxix., 322). For instance, the stereomeric sodium β -chlorocrotonates heated with alcoholic sodium ethylate give the fum. ethoxy-derivative. Each of these chloro-salts lose HCl readily under the conditions of the experiments and form the tetrolate, which should pass over, as such acetylenic derivatives add alcohol easily in the presence of ethylate, by trans-addition into the fum. β -ethoxycrotonate.

We can now explain why these β -chlorocrotonates with alcoholic sodium ethylmercaptide give stereomeric thio-derivatives (Autenrieth, *Ann.*, 1889, ccliv., 222). Ethylmercaptane is decidedly more acidic than ethyl alcohol, and the mercaptide for this reason is much less basic, and therefore less capable of splitting off HCl from the salts; further, the additive capacity of the mercaptide to Δ -carbon atoms is much greater than that of the ethylate. On account of these properties the primary action of the mercaptide is to unite with the Δ -carbons, and then, whether the displacement of halogen in the saturated derivatives thus formed proceeds by substitution or by elimination and subsequent addition, stereomeric β -thio-ethoxy compounds must be formed.

Evidently, the use of such synthetic reactions to establish the configuration of unsaturated compounds is of doubtful value when the structures of the simpler compounds are such that the hindrance to reaction by elimination and addition is less than to direct substitution, and the results should only be used in confirmation of stereo-structures, which are ascertained by more certain methods.

Anhydride Formation.—Van't Hoff explained the facile anhydridisation of the maleinoid, ethylenic dibasic acids by the spacial nearness of their carboxyl groups, in comparison with those in the fumaroid forms. A closer analysis leads to the conclusion that the main contributory cause is the slight hindrance to the formation of five-membered rings from groups in the cis-position owing to the proximity in space of certain atoms in positions one and five. In every respect the anhydride corresponds to the lactone formation (Michael, *Journ. Prakt. Chem.*, 1899, [2], lx., 338), and provided a less resistance to the course of a decomposition in another direction does not exist, the effect of heat on all such hydroxy and dibasic acids should lead more or less readily to the formation of lactones or anhydrides. That the fumaroid acids do not yield anhydrides by physical or chemical means is not because of the impossibility of a fumaroid anhydride, but because the resistance to a transmutation into the corresponding maleinoid configuration of the acid with subsequent dehydration is less, and therefore the energy required is less than in the direct anhydride formation. Indeed, such fumaroid anhydrides would be bodies of slight stability, and owing to the great strain existing in the fumaroid rings they would pass over, more or less readily, into the maleinoid forms.

The phases in the lactone formation from γ - and δ -hydroxy acids are the addition of hydroxyl to carbonyl, and then the loss of water; that is, in this case an intramolecular esterification (Michael, *Ibid.*; *Ber.*, 1909, xlii., 312); and the formation of an acid anhydride, irrespective of the basicity of the acid, proceeds in a similar manner.



Here, too, the carbonyl oxygen and the acidic hydrogen are the atoms with the greatest free energy content that may be involved in the change, and which have the requisite affinity relations.

The chemical factors that increase the facility of this ring formation are—(1) constitutive changes causing spacial approach of the involved carboxyls, and (2) those which reduce the affinity of the hydrogen to the oxygen of the hydroxyl, and the additive capacity of the respective carbonyl for that group, since with each change the intramolecular addition process is facilitated. Replacing a nuclear hydrogen in maleic acid by a methyl group increases the bound energy of the remaining nuclear cis-hydrogen and of the carboxyls, causing increased segmentation of the axial carbons, and with it ease of anhydride formation (Krafft, *Ber.*, 1895, xxviii., 2588; 1904, xlii., 214; Fittig, *Ann.*, 1899, ccciv., 124 and 145) (52); repetition of the chemical change gives in pyrocinnic

acid a substance that decomposes spontaneously into anhydride and water. The successive replacement of the nuclear hydrogens by halogens also favours anhydri- sation, because the free energy in halogen and hydrogen or that in two halogens (Michael, *Ann.*, 1912, cccxc., 47), which are here in cis-relations, tend to neutralise each other spatially, and particularly because halogen greatly increases the additive capacity of carbonyl for water (Michael, *Ibid.*, 1908, cccxliii., 32, footnote 25) (53).

Stereo-mutation (54).—Even after the radical difference presupposed by van't Hoff between the spatial relations in the axial carbons of saturated and unsaturated derivatives had been experimentally disproven (Michael, *Journ. Prakt. Chem.*, 1892, [2], xlv., 209, 425) (55), various attempts were made to explain stereomeric introconversions in the latter group on that basis as well as upon such hypotheses as the intermediate formation of α -lactones (Liebermann, *Ber.*, 1890, xxiii., 2513; 1895, xxviii., 1444), which are unknown and could not possibly show the properties assumed for them, or that of intermediate tetramethylene derivatives (Stewart, "Stereochemistry," 1907, p. 189), which are known but show properties incompatible with the suggestion.

The behaviour of stereomers, and that of other classes of substances, towards heat energy are essentially alike. For instance, barium oxide and carbon dioxide are inert at a very low temperature; under ordinary conditions they unite with loss of free chemical energy and heat, and at a certain higher temperature the barium carbonate thus formed must either volatilise or decompose into barium oxide and carbon dioxide, with absorption of heat and increase of free energy. Likewise, heat energy enables maleic acid to overcome the hindrance and pass over with loss of free chemical energy and heat into fumaric acid, which at a sufficiently high temperature must either, with increase of free energy, volatilise, decompose, or be transmuted into maleic acid (Anschutz and Wirtz, *Ber.*, 1885, xviii., 194). In one case the change is inter-, in the other intramolecular, which is characteristic of stereomeric changes, as is also the fact that largely in consequence, generally speaking, they take place within a comparatively small range of temperature.

Evidently, any structural modification in a mal. derivative which decreases the bound energy between the atoms in the axial groups, *i.e.*, decreases the segmentation of the axial carbons and at the same time increases the free energy, must facilitate stereo-mutation. For instance, replacing the hydroxyls of maleic acid by chlorine, enhances the free energy, while it decreases the bound energy that existed between the carboxyls, and in striking contrast to maleic acid its chloride passes over slowly at ordinary temperature into fumaryl chloride (see Michael, *Am. Chem. Journ.* 1908, xxix., 5, for explanations of the effects of physical influences). Or allo-8-chlorocrotonic acid (94²) is only partially stereomerised at 164° (Michael and Schulthess, *Journ. Prakt. Chem.*, 1892, [2], xlv., 265), but at a much lower temperature its chloride in one distillation is completely stereo-mutated (Autenrieth, *Ber.*, 1896, xxix., 1665).

Delisle (*Ann.*, 1892, cclxix., 74) has shown that heating aqueous sodium citraconate, even up to 190°, gives only traces of the mesaconate; but an excess of caustic soda causes the conversion at 100°, and with a velocity increasing with the concentration of the alkali; further, that the transmutation is reversible. It was explained above why the considerable difference in the free-energy relations of the corresponding acids disappears with their conversion into salts, which is evidently connected with the pronounced stability of the citraconate. To effect a change more readily chemical energy must be added to the system, which is done by the excess of alkali uniting to form either basic salts or "polymolecules," whose stability in solution should increase with the excess of the base. Further, it is evident that the energy relations in the salts favour a balanced reaction.

A further discussion of stereo-mutation is beyond the

scope of the paper; it may be mentioned, however, that as great confusion exists here as in any other field in stereo-chemistry. This is due in part to the frequent use of untenable theoretical conceptions, and to the fact that it is the dumping ground for any pair of easily introconvertible compounds, no matter how improbable it is that they are stereomeric in the usually accepted sense.

Notes.

51. In connection with considerable experimental material see *Journ. Prakt. Chem.*, 1899, lx., 414; *Ber.*, 1895, xxviii., 2512; 1896, xxix., 1792.

52. Since the accumulation of alkyls near hydroxyl and carboxyl groups favour ring formation, possibly fumaroid lactones and anhydrides may be obtained from poly-alkylated derivatives. Although dimethylfumaric acid and acetyl chloride at 100° give pyrocinnonic anhydride, perhaps a fum. derivative may be obtained from the silver salt and the reagent at a lower temperature; or from dialkyl fumaric acids where the alkyls are sec. or tert. radicals.

53. Owing to the affinity of such very negative carbonyl for water the anhydrides of these dihalogen acids very likely pass back in aqueous solution to a more or less extent, into the dihydroxy lactones through which they are formed in the anhydri-sation of the free acids. Wegscheider (*Ber.*, 1903, xxxvi., 1543) considers it probable that pyrocinnonic anhydride goes partly over in solution to such a compound, which also is not unlikely, as the accumulation of alkyl groups about a carbon likewise favours its affinity for hydroxyl (Michael, *Journ. Prakt. Chem.*, 1899, [2], lx., 423, footnote 4; 1902, xlv., 108).

54. This word is suggested in place of stereotransmutation.

55. In his "Lehrb. d. Stereochemie" (1904, p. 222) Werner makes the historically inaccurate statement that Anschutz (*Ann.*, 1889, ccliv., 174) and Fittig (*Ibid.*, 1890, cclix., 30), first, then Skraup (*Monatsh.*, 1891, xii., 107) called attention to the impossibility of the Wislicenus transmutation explanation, which was based on the instability of addition products that in reality are stable, and then Michael (*Journ. Prakt. Chem.*, 1892, [2], xlv., 209) proved it experimentally in numerous cases. This inverted order of priority, which is frequently met in the literature, is due to the oversight of the above-mentioned chemists that in the writer's first criticism (*Ibid.*, 1888, xxxviii., 21) of the Wislicenus hypothesis practically all the reasons advanced later by them against that chemist's interpretation are clearly stated, and given in proof of its untenability.

(To be continued).

KIMBERLEY DIAMONDS: ESPECIALLY CLEAVAGE DIAMONDS.*

By J. R. SUTTON, M.A., Sc D., F.R.S.S.A.

(Continued from p. 47).

10. Broken Diamonds.

THE origin of the numerous broken fragments of diamond is somewhat of a mystery. G. F. William (p. 492) remarks that—"Some observers claim that the broken diamonds which are extracted are broken during the process of winning them. It is admitted that diamonds may be broken in the process of mining and the subsequent operations of winning, but these cases are exceptional. Fragments of diamonds are very frequently found embedded in the blue ground, and there is no doubt in the mind of anyone who has had practical experience in finding these fragments that they were not crystallised where they are found." On the substructure of this

* From the Transactions of the Royal Society of South Africa, vii., Part I.

evidence Wagner (p. 164) and Bauer (p. 195) assign the origin of Kimberley diamonds to a deep-seated plutonic rock, claiming that the broken fragments owe their condition to violent eruptive outburst which shattered country, rock, and blue ground alike (*Cf.* also L. J. Spencer in "The World's Minerals," page 46, 1911). The latter, however, stultifies his argument to a certain extent in his very next paragraph, where he states that the minerals and rock fragments in the blue ground show no signs of wear and tear. It is hard to see how the diamonds could have suffered so much damage and their kimberlite surroundings none at all. As a matter of fact, better authorities tell us that the rock fragments in the pipes do show a great deal of wear and tear. (See A. L. du Toit "Geological Survey of the Eastern Portion of Griqualand West," in the Eleventh Annual Report of the Cape Geological Commission, 1906). Du Toit, it may be noted, provisionally accepts the theory that the shattering of the kimberlite accounts for the fracturing of diamonds, but observed that garnets have not suffered to the same extent (p. 151).

11. Spontaneous Breaking.

A more attractive theory, and one repeatedly quoted from one to the other by writers on the diamond, is that certain classes of diamonds frequently tend to break of themselves. G. F. Williams (p. 500) is responsible for the opinion that "light brown, smoky diamonds often crack on exposure to the dry air, but they will remain intact if kept in a moist place. The cracking is, therefore, more probably the result of heat or drying than of tension or inward (? interior) pressure. It is possible, however, that the great heat to which the diamond is exposed when brought to the surface may expand contained gases sufficiently to crack the stone." Crookes, on the other hand (Kimberley Lecture), seems to attribute the fractures to sudden lowering of pressure in the space surrounding the diamonds, and speaks of consequent explosions. G. H. Smith (p. 131), following Crookes, says that "so great is the strain that many a fine diamond has burst to fragments on being removed from the ground in which it has lain."

Unfortunately, the evidence for this particular theory, as a complete theory, is not strong nor very extensive. What, at first sight, might look like a consensus of scientific opinion is, in reality, gossip handed on from one to the other by nearly all, and is by no means the outcome of independent research. Personally, I have met plenty of people who have heard of the bursting of smoky diamonds without ever having witnessed such a disaster with their own eyes, and the story of the custom of sending them to England inside potatoes is almost a chestnut. Certainly the De Beers Company never pack any of their millions of diamond in potatoes. A possible case of spontaneous breakage is known in the De Beers' sorting-office, and another, in which a crack was found in a diamond where no crack was observed—and the chances are, did not exist—before. Besides this, there are many brown and other fragments which do possess very fresh-looking cleavage faces, and so might have done as the frog did in the fable.

And then there is the deduction from the statistics, previously remarked upon, that the proportion of brown cleavages to brown stones is unduly high. All this hints at the possibility of some measure of early or late spontaneous disintegration, but no more. Moreover, a great many broken diamonds are not brown or smoky at all. Anyway, diamonds do not explode of themselves under meteorological conditions. It is said that certain philosophers, acting under the orders of the Grand Duke of Tuscany, once caused a diamond to explode by exposing it to the sun's rays in the focus of a powerful lens two-thirds of a Florentine ell in diameter; but in this case, since the diamond was of a good size—nearly ten carats in weight—the result might have been caused by unequal heating rather than by the terrific heat alone.

If heat will not cause a diamond to shiver (!) according

to Crookes, and moisture will prevent such a catastrophe according to Williams, it is not easy to understand what any "cunning dealer," wishing to buy but taking no unnecessary risks, has to gain by encouraging sellers to handle their goods freely or carry them in their warm pockets, which is what we are told the cunning dealers do; and cunning indeed they must be if they can so contrive, and foolish the seller who could be so circumvented.

(A few experiments have been made with the object of ascertaining whether a moderate heating, up to a temperature of 100° C. in water, will create strain in a diamond or vary a strain already there; but with no proof as yet that it can).

It is to be suspected that much of the myth that has collected round the nucleus of an occasional accident to a smoky diamond is derived from the old story of Albertus Magnus, that a diamond immersed in the fresh, warm blood of a goat (especially if the animal had previously browsed on parsley or drunk wine) would burst. Pliny, it will be remembered, had a similar idea—namely, that the blood of a billy-goat had power to lessen the molecular cohesion of the adamas stone, which stone seems to have been diamond but may have been something else: "The blood, however, must be no otherwise than fresh and warm; the stone, too, must be well steeped in it, and then subjected to repeated blows; and even then it is apt to break both anvils and hammers of iron if they be not of the finest temper" (xxxvii., 15).

With reference to the hypothesis of heat causing a diamond to break or explode when it is brought to the surface, the highest temperature to which it would be subjected above ground would be experienced on the depositing floors under the sun's rays, say about 60° C. (140° F.). The temperatures underground at the greatest depths yet reached are not so high as this, probably not touching 40° C. A large flow of water met with in the main rock tunnel at a depth of 1525 feet in the Kimberley Mine had a temperature of about 30° C. (84° F.).

The theory that diamonds were broken by violent movements of the kimberlite does not explain the cause of the breakages among diamonds found in gravels, unless we may conclude that these diamonds were brought to the surface in outbursts of plutonic energy. Perhaps they were not so brought.

Again, a yellow diamond recently examined, having a very striated surface which prevented its interior from being properly seen, showed a crack running half the way round the outside of the stone. The polariscope indicated a great state of strain somewhere near the centre of the stone at a place where the crack seemed to extend inwards to. Now, if the expansion of contained gas had caused the stone to split, the gas must have escaped through the crack. Why, then, the continued strain? Again, where could the internal strain have come from if the stone had been broken by concussion in machinery or pipe? The De Beers Company has a diamond with a percussion figure like a clock-face under its surface, and in this case the shock which made the figure has set up no internal strain. We shall see in the following section how the strain and crack in the above yellow diamond have probably arisen.

12. Suggested Reasons for Breaking; Mineral Inclusions, &c.

The suggestion now to be put forward, with all deference to better authorities, is that the circumstance of broken diamonds on a large scale is not alone due to:

1. Either the spontaneous breaking up of those that are smoky or brown, or any other colour;
2. Or to breaking in the process of mining and winning;
3. Or to violent movements of the kimberlite in past time;
4. Or to the expansion of contained gases within the diamonds whether by heating or relief of pressure outside,

though each or any of these actions may have been of some effect; but principally to the energy exerted by the mineral inclusions so often contained in diamonds. These inclusions are most frequently garnet, and there are, besides, zircon, ilmenite, iron pyrites, and (possibly) chrysolite—or enstatite: "A bright green variety occurs in large cleavable fragments in the diamond-bearing detritus of Colesberg Koppje in the Transvaal!"—H. Bauerman, "Text-book of Descriptive Mineralogy," 1897; some of this material is harder than window glass. There are also inclusions of what may loosely be called *sploches* of graphite (very numerous), oxide of iron, and chrome diopside (rare). Some of the black inclusions may be either ilmenite or hæmatite, or graphite, but they are so small that specific gravity tests (the only tests that are available without breaking the diamond) are not delicate enough to determine which. Diamonds possibly tinted by diopside have turned up now and then; but only one hitherto in our mines, containing a definite splotch of the material. But some years ago a beautiful specimen of a diamond was found in the Voerspoed Mine (O.F.S.), which contained a number of bright green splotches, doubtless diopside. This stone is now in the possession of G. F. Williams, and is probably peerless of its kind for beauty. A genuine crystal of chrome diopside has yet to be found in a Cape diamond; although it has been met with in bort.

Bauer (p. 192) states that "until recently no diamond had ever been observed attached to another mineral in such a way as to suggest that the two grew side by side at the same time. The discovery, however, of a diamond crystal attached in this way to a garnet shows that such a growth does take place, though rarely." This assertion besides being bad science is bad history. The phenomenon is neither rare nor new. Evelyn relates in his diary how on Michaelmas Day, September 29, 1645, he visited the collection of the noble Venetian Signor Rugini, where he saw "above all a diamond which had a very fair ruby (? garnet) growing in it."

In the majority of cases the garnet, or other inclusion, is not actually inside the diamond, but is set more or less deeply in a cleavage face. Also a very great number of cleavage fragments contain somewhere in their fractured surfaces small rounded holes or indentations such as could scarcely arise in breaking unless the holes or indentations had been there first, with something inside them. This latter circumstance indicates that diamonds containing inclusions have been more frequent in nature than we should infer from even the considerable number found with the inclusion present. Some of these holes may possibly have contained gas or liquid.

In trying to interpret the facts we have to bear in mind that the thermal expansion of pretty well all crystals, saving those of the beryl family, at ordinary temperatures, is much greater than that of the diamond. Between 0° and 100° C., for example, the coefficients of cubical thermal expansion are for:

Zircon	0.2835
Garnet	0.2543
Quartz	0.3530
Diamond	0.0354

Whether these relative values would hold under plutonic conditions of heat and pressure is perhaps uncertain, though the coefficient of thermal expansion for diamond is said by Miers to increase rapidly at high temperatures and to diminish rapidly at low ones. For our present purpose very high temperatures need not concern us; nothing higher in fact than the comparatively low temperature at which garnets fuse, since there does not appear to be any evidence that the garnets of the Kimberley Mines have ever attained this temperature. "One character," says Church ("Precious Stones," p. 64), "common to all garnets save Uwarowite is their fusibility before the blowpipe; they thus yield a vitreous mass which is of much lower density than the original garnet before

fusion." This refers to experiments in air, of course, and things may be somewhat different under pressure deep down in the earth. In any event, the garnets of our mines have probably not been subjected to very high temperatures because none seem to have been found of the requisite low specific gravity. Kimberley garnets vary in specific gravity, it is true, but none tested in the De Beers office have been anything like so low as 3, the value for vitreous garnet. We shall, doubtless, be on the safe side in assuming that the thermal expansion of garnet, zircon, &c., under temperature conditions that are reasonably probable, is always greater than that of diamond, though not necessarily greater by a constant multiple.

Two alternatives are conceivable. First suppose a diamond to have crystallised about a foreign body, such as a garnet, and that at some subsequent time there was an increase of temperature in the surrounding magma. It is clear that a greater relative expansion of the inclusion would put the diamond into such a state of strain that, if the magma were not solid, the diamond might give way and break. That there has been such an elevation of temperature is rendered not improbable by the large number of diamonds showing signs of corrosion (?Luzi's figures), and by the coatings of graphite on others; possibly also by the phenomena of flaked diamonds. In the De Beers collection is one of these, a stone the greater part of which is in thin opaque grey laminae, like an oyster-shell (the crystalline part of this diamond is a non-conductor of electricity, but the laminated part conducts as well as bort). The state of this diamond was for a long time erroneously attributed to shattering by dynamite, but it is more likely to have been caused by overheating in the pipe during some past time. Many Premier diamonds, also, show incipient local flaking ("feathers") on their surfaces. Some of the diamonds belonging to the Emperor Francis I. are said to have split into thin flakes when heated in a crucible. Elevation of temperature may also be indicated by the opaque white material, unaffected by hydrofluoric acid, occasionally found in local patches on diamond surfaces. Quite a large area of a certain lump of black bort from the Premier Mine was thus covered. A similar-looking stuff—perhaps the same—occurs, however, in some of the cavities in the cleavage faces of diamonds and round enclosed garnets, which makes it difficult to understand how it could be produced by heating; for the heat required should presumably have destroyed the diamond surface outside before it could reach the cavity.

Another guess that might be made is that the diamond crystallised about the garnet at some pretty high temperature, and that the relative expansion of garnet as compared with diamond was less than it might have been at some later lower temperature. In this case it would be the cooling as plutonic activity died away that would set up the fracturing.

Whether we accept either alternative or neither, it is certain that diamonds do cleave freely across foreign crystal inclusions. Here is a case in point. A very fine diamond, weighing 42 carats and valued at over £600, was recently found in the Wesselton wash. It is a fair-shaped octahedron, as Cape octahedra goes, and is much indented with the shallow triangular depressions characteristic of its mine. It contains the most lovely inclusions one can imagine—one apparently a small garnet, another a honey-coloured zircon, just deep enough in colour to show, very faintly, two colours in the dichroscope, of fair size. Through, and surrounding the position of, the supposed garnet is an extensive crack, while both above and below the zircon, and tangential to it, are similar cracks. These cracks are parallel to contiguous faces of the diamond, and neither reaches the surface of the latter. (In another, similar, case the cracks did reach the surface). The zircon with the two parallel cracks touching it exhibits an odd resemblance to an airplane in flight. Under the polariscope a state of great internal strain is manifested over a large area in the region

of the zircon by a most magnificent coloration, while the zircon itself is equally splendid. Words indeed are insufficient to describe the chromatic beauty of the polariscopic view. Curiously, there appears to be no strain to speak of in the vicinity of the crack through the garnet, as though the strain which once must have existed there and caused the crack had been relieved.

Of course, one would expect more strain in general about a zircon inclusion than about a garnet one because of the somewhat greater coefficient of thermal expansion of the latter, especially along one of its crystal axes. This outstanding specimen illustrates very well the force of the two alternatives mooted above. For as internal strain still persists in spite of the present moderate temperature of the stone, it would appear that either the diamond must have crystallised at a surprisingly low temperature or at some high one at which its coefficient of thermal expansion must have been relatively greater, compared with that of the zircon, than it is now.

Arising out of the condition of the specimen in question an interesting point emerges—

Some broken diamonds, as we have said, show rounded holes in their cleavage faces, but others do not. Now we cannot conclude that those which do not show the holes were not broken by the expansion of a foreign mineral inclusion; for if the cracks bounding the zircon in our specimen were to spread outwards all round to the diamond faces, it looks as though, from their position, neither of the two outer fragments, of the three into which the diamond would break, would show signs of holes. Thus, even when a cleavage surface exhibits no imprint of a former mineral inclusion, it does not follow that the cleavage was not caused by an inclusion. It may be surmised, in passing, that the cracked yellow diamond spoken of in the last paragraph of Section 11 contained a mineral inclusion. (But diamonds suffering strain, and with visible internal cracks, though apparently containing no inclusion, are sometimes met with).

The remarks in the present section apply in the main to more or less transparent diamond. Opaque diamond, other than bort, often enough is flawed, has little cohesion, and can be easily broken.

13. Diamond Inclusions.

Diamonds enclosed in diamonds are not exactly uncommon. There are two very fine, nearly white, fair-shaped octahedra preserved in the De Beers office, each containing an inclusion. Both inclusions are practically of the same colour as their enclosures—one, a rounded octahedron, is certainly a diamond; the other is probably a diamond, but may be something else—say, quartz as a remote possibility. These diamonds show very fine colour effects under the polariscope, but neither is much flawed internally. Where the strain comes from, though, when one diamond encloses another is an enigma.

Inclusions of diamond in diamond are not often symmetrical octahedra. One which was almost perfect in outline has been referred to in Section 4. A full description of this interesting object, which is still preserved, has been given by Williams (p. 506). The majority of such inclusions are irregular. A certain piece of Bultfontein cleavage, for example, which came from the wash already cracked nearly through was found, when broken up, to contain a venerable looking and ill-shapen flake of diamond, the cavity in which it had been being lined with a soapy-looking substance, possibly apophyllite. In this connection it is strange that the apophyllite, or whatever the substance may be, prefers to stick to the enclosure and not to the inclusion. Pretty often in cases of this sort the portions of diamond separated by the crack are of different quality and colour.

Tiny cavities, or what look like cavities, in diamonds are not uncommon. They may contain gas. It is not the rule to find any large amount of mechanical strain in their vicinity.

(To be continued).

FALLING PRICES OF MATERIALS.

THE report of the Committee of "Financial Risks attached to the holding of Trading Stocks" is now published by the Ministry of Reconstruction. The Committee were appointed early last year by Dr. Addison, who recognised that fear on the part of manufacturers and traders of losses, due to a fall in prices of raw material bought at war time prices, would tend to cause a reluctance to embark on full-scale production after the War and would thereby retard the attainment of maximum national productivity. He accordingly invited the Committee to enquire and report as to any measures which could be adopted with a view to securing that manufacturers and others should be financially in a position to hold stocks after the War, and that reasonable safeguards should be established to prevent serious financial losses as a result of possible depression following on a period of great inflation, in respect of stocks of materials required for industry.

After illustrating the enormous rise during the War in the prices of raw materials and goods, the Committee express the view that apprehension of loss due to a drop in prices is well founded. Five main causes are likely to bring about this fall:—

1. The disappearance of War Risk insurance, &c.
2. Reduction in freights due to increased availability of shipping.
3. Fall of wages compared with the rates prevailing during the war due to increased availability of labour on demobilisation.
4. Additional production (due to cessation of the demand for military material) of staple articles now standing at "scarcity prices."
5. Reduction of the note issue to restore an effective Gold Standard, or in other words, "deflation" of credit.

A natural corollary of the trader's fear that he will lose through falling prices is that he should wish to take a very conservative valuation of his unsold stock. This affects their valuation for the determination of excess profits duty.

The three lines of possible relief that have been suggested by traders are—

1. Lower rates of taxation during the War.
2. The Government to bear a share (out of taxes already received) in any losses after the War.
3. A redefinition of "profits" now chargeable to taxation by way of permission to create reserves before arriving at the sum chargeable to taxation as profits, or by the adoption, when making up periodical accounts, of different principles of valuing stocks from those generally obtaining in industry hitherto, or admitted by the taxing authorities.

Up to the present taxation relief has been granted by two concessions contained in the White Paper (Cd. 8623), viz.,

1. An allowance is made for the fall in the value of stocks held in the last accounting period, to the extent to which they are realised in the succeeding two years.
2. The "Base Stock" method of valuation, i.e., that of valuing a constant quantity of stock at a constant price which is permitted in certain classes of industry wherein it is a practice of the Trade.

The first concession is criticised as being (1) Unworkable, because the physical identity of the stock sold cannot in practice be ascertained, and (2) Inadequate, as relating to only one set of sales. Only a very limited number of industries have obtained the second concession. Those which have done so will commence the post-war period with stocks valued considerably below

their market price, and therefore, in the opinion of the Committee, have established no further title to relief.

Suggested Remedies.

The Committee (preface their general recommendations by saying they) regard it as most desirable that the position of industry should be specially strengthened when on the threshold of a period in which markets have to be reorganised or created, and in which industrial conditions are in the highest degree uncertain. The most hopeful line of approach to a solution of this problem lies, they think, in a reduction of the present rates of excess profits duty. The present 80 per cent duty, they consider, encourages extravagance and discourages enterprise, the reward being paltry, while little margin is left for renewals, development, and the capture of new markets, to say nothing of the establishment of reserves against bad times.

The Committee recommend two alternative remedies—

1. A reduction in the Excess Profits duty from 80 per cent to 65 per cent for the accounting period approximating to the year 1918 now in course of assessment, on the understanding that the duty so remitted is retained in the business and not distributed. This reduction might be accompanied by the withdrawal of the first concession in the White Paper, which was largely a result of the raising of the duty to 80 per cent.
2. If this course is impracticable, the Committee suggest that part of the duty now to be paid should be treated as a suspensory reserve for a period of five years, the amount so treated to be represented by a special kind of War Loan to be held on joint account by the Government and the taxpayer. The amount of this reserve should be 20 per cent of the average excess of profits in the last two years of the duty. After five years this reserve should either revert finally to the State, or in the following circumstances become wholly or in part the property of the taxpayer.

He must show that his annual profits over that period are less than the amount of the percentage standard to which he was entitled or would have been entitled under Excess Profits duty, and that these deficiencies have been associated with the holding, during this period, of stocks at falling prices as distinct, for example, from bad management or reduced turnover. He would then be entitled to relief to the extent of 80 per cent of the deficiency; but for no greater sum than the amount of the reserve.

In the case of the second remedy the Committee consider that the undertakings given in the White Paper should continue to stand and that each business should state, when making its return for assessment for the last period of excess profits duty whether it proposes to come under the first concession in the White Paper, or, waiving all rights thereunder, to come under the five year War Loan system of relief.

A reservation by four of the ten members of the Committee expresses the view that the "base stock" method of valuation should be permitted by all traders, but that the valuation prices must not be lower than they have actually been within the trader's experience. Further, they are of opinion that if the suggested remedy by way of reduction in the duty cannot be granted, the amount of the reserve allowed in the second remedy should be at least double.

The Committee recognise that they have been unable to formulate any scheme of relief for those who pay no Excess Profits Duty. They also consider that a business which has denuded itself of its "immanent stock," at the instance of the Government, to meet immediate needs, has a claim for consideration which is best preferred to, and granted by, the Department of State to which the assistance was rendered.

NOTICES OF BOOKS.

Treatise on Applied Analytical Chemistry. By Prof. VITTORIO VILLAVECCHIA. Translated by THOMAS H. POPE, B.Sc., A.C.G.I., F.I.C. Volume II. London: J. and A. Churchill. 1918. Pp. xv+536. Price 25s. net.

IN the second volume of this treatise a very wide range of subjects is covered, including meat, milk, flour, sugars, alcoholic liquids, essential oils, varnishes, rubbers, colouring matters, textile fibres, &c., and although the book is bulky only a comparatively small space can be given to each subject, with the result that the treatment is in some cases rather deficient as regards detail. The methods selected for description do not appear to have been always very well chosen, sometimes perhaps because Italian practice is not entirely in accord with that adopted in this country, although in some cases the text has been slightly modified on that account, and the section on beer, for example, has been practically rewritten for the English edition. In the section on milk no mention is made of the Werner Schmidt process, nor are any of the widely adopted modifications of Kjeldahl's process mentioned. The sections on the organic colouring matters and their identification on woollen and cotton materials are somewhat too much compressed to serve as really useful guides in analyses, whilst on the other hand, for completeness sake, some comparatively unimportant substances have been included. Nevertheless, the author and his collaborators may be congratulated upon having produced a work which achieves a considerable degree of success, and in which many difficulties have been surmounted.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxvii., No. 17, October 21, 1918.

This number contains no chemical matter.

No. 18, October 28, 1918.

Inversion of Cane-sugar by Colloidal Silica.—Albert and Alexandre Mary.—Colloidal silica was prepared chemically by the action of hydrochloric acid upon sodium silicate, and its action on cane sugar studied. Like mineral acids, acetic acid, hydrosols of palladium, &c., it causes an appreciable amount of inversion. In some circumstances its activity increases with the temperature up to a variable optimum (below 100° C.), and then decreases until it becomes completely inactive. In some respects the conditions of its activity are comparable with those of the colloidal metals, but no chemical reason can be given for this resemblance.

No. 19, November 4, 1918.

This number contains no chemical matter.

MISCELLANEOUS.

Royal Institution.—Next Tuesday, February 4, at 3 o'clock, Prof. J. T. Macgregor Morris will deliver the first of a course of two lectures at the Royal Institution on "Study of Electric Arcs and their Applications." On Thursday, February 6, Dr. W. Wilson will give the first of two lectures on "The Movement of the Sun, Earth,

and Moon" (illustrated by a new Astronomical Model). The Friday evening Discourse on February 7, at 5.30 will be delivered by Prof. J. G. Adams on "Medical Research in its Relationship to the War"; on February 14, by Prof. Cargill G. Knott on "Earthquake Waves and the Interior of the Earth."

Methane.—William Malisoff and Gastave Egloff.—The authors have brought together the results of investigations upon methane, including the physical characteristics and chemical properties, and its synthesis and decomposition. A very useful part of the paper deals with research possibilities on methane. Many suggestions are made as to subjects and details which demand further or new research; these include the checking of some of the physical constants, oxidation, nitration, and sulphonation, the formation of derivatives by electrical methods, and the reactions of methane in the silent discharge with nitrogen, carbon monoxide, and various other substances. In all 53 different researches are tabulated, and some of them, if successfully accomplished, might lead to results of considerable practical utility.—*Journal of Physical Chemistry*, vol. xxii., No. 8, p. 529.

MEETINGS FOR THE WEEK

MONDAY, Feb 3rd.—Royal Institution, 5. (General Meeting).

TUESDAY, 4th.—Royal Institution, 3. "Study of Electric Arcs and their Applications," by Prof. J. T. MacGregor Morris.

— Röntgen Society, 8.15. "Protection in Diagnostic Work—a Consideration of the Effects of Scattered Rays and Secondary Rays," by Capt. F. Herniman-Johnson. Lieut. W. Makower will exhibit and describe a Langmuir Exhaust Pump.

WEDNESDAY, 5th.—Society of Public Analysts 8. (Annual General Meeting). "Recovery of Nessler Reagent," by D. Pullman. "Technique of Iodine Determinations, with a Note on a New Machine for Subdividing Oleaginous Seeds," by J. Allan.

— Royal Society of Arts, 4.30. "The Removal of the Residual Fibres from Cotton-seed, and their Value for Non-textile Purposes," by Edward Carstensen de Segundo.

THURSDAY, 6th.—Royal Institution, 5. "The Movements of the Earth, Sun, and Moon," by Dr. W. Wilson.

— Royal Society, 4.30. "The Elasticity of Metals as Affected by Temperature," by A. Mallock. "Vibration and Strength of Struts and Continuous Beams under End Thrusts," by W. L. Cowley and H. Levy. "A New Method for the Absolute Determination of Frequency" (with a Prefatory Note by C. V. Raman), by A. Dey.

— Chemical Society, 8.

FRIDAY, 7th.—Royal Institution, 5.30. "Medical Research in its Relationship to the War," by Prof. J. G. Adams.

SATURDAY, 8th.—Royal Institution, 3. "The Works of J. S. Bach," by Prof. H. P. Allen.

FRANCE (BORDEAUX and SUD-OUEST).—Representations wanted by French Engineer Chemist of good firms (for Chemical Products, Chemical Machineries, Chemical Apparatus, New Processes).—Address TEYSSEIER, 301, Cours Balguerie, Bordeaux.

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Director of Education
City Hall, Cardiff.

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ELECTROLYTIC DISSOCIATION.*

By S. ARRHENIUS.

1. *Evidence from Analytical Chemistry.*—There are four fundamentals upon which the idea of a dissociation of electrolytes (*i.e.*, salts, acids, and bases) into their ions is built up. These four are the additive properties, the electric conductivities, the freezing-points, and the catalytic actions of electrolytes. That which has won the adhesion of most chemists is the rational explanation of analytical chemistry which is here given. All salts which belong to the group of chlorides give the same reactions which in olden times were said to be characteristic of chlorine. The most familiar of these reactions is that with any silver salt in aqueous solution—in most cases silver nitrate is used for analytical purposes—which gives a characteristic cheese-like precipitation of silver chloride. But it is not true that the said reaction is characteristic of all substances containing chlorine; for instance, chlorates, perchlorates, a great number of inorganic chlorine-containing compounds of metal, examined by Werner and his school, as well as most organic chlorine compounds, do not show this characteristic reaction. All the chlorine compounds which show it are characterised thereby in that, on being electrolysed, they give chlorine as an ion; the other chlorine compounds are either not conductors of electricity when dissolved in water, or, if they are, they do not give chlorine as an ion.

This peculiarity was absolutely inexplicable on the old chemical theories, and there is no other explanation than that salts, and in general electrolytes, when dissolved in water, alcohol, or another solvent, are partially decomposed into their ions, *e.g.*, sodium chloride into sodium ions and chlorine ions, and that each ion has its own characteristic reaction.

Also a very well known fact of quantitative analytical chemistry speaks in favour of the dissociation theory. The characteristic reagents for barium salts are sulphates, which give a very little soluble precipitate, barium sulphate, when they are added to an aqueous solution of a barium salt. The analytical chemist, who wishes to precipitate the dissolved barium as completely as possible, adds his sulphate solution in excess. The barium sulphate is the less soluble the greater the content of sulphate ions in the solution. This behaviour can be explained only in the following manner. The barium ion and the sulphate ion in the mixed solutions give barium sulphate, with which they are in equilibrium. This barium sulphate is only soluble to a certain degree at a given temperature; the excess becomes precipitated. This quantity of barium sulphate may exist in a solution in presence of a certain quantity of sulphate ions and of barium ions, but the greater the quantity of the sulphate ions present the less is the quantity of barium ions in the equilibrium. The barium ion is therefore precipitated by the sulphate ion the more completely the greater the quantity of sulphate ion added. Evidently this equilibrium between barium-sulphate barium-ion in the solution and sulphate ion cannot be understood if the barium ion and the common constituent of all sulphates, SO_4 , are not free from each other.

In reality the theory of electrolytic dissociation has furnished analytical chemistry with a leading principle which it missed before. The great practical importance of chemical analysis gives the strongest support to the theory of electrolytic dissociation.

2. *Additive Properties.*—The aforementioned behaviour of electrolytes is a special instance of the so-called additive properties of this important class of substances. These additive properties had for a long time attracted the attention of physico-chemists. Valson in 1870 showed that the capillarity and the specific gravity of a salt solution might be regarded as the sum of three characteristic magnitudes, the first valuable for the solvent—he used water as solvent—the second for the positive ion (metal) of the salt, and the third for its negative ion. Such additive properties have been investigated in great numbers, as may be seen from any text-book of physical chemistry, and in general it may be maintained that any property of a dilute solution is additive. The solution behaves as if it contained, besides the solvent, two independent substances—the metal ion of the salt and its negative ion (the rest of the salt).

Amongst these properties there was one which had interested chemists in a high degree, namely, the heat evolved on the formation of a salt in a mixture of the dilute solutions of the corresponding basis and acid. If these are strong, the said heat is 13.4 great calories per grm.-equivalent. The well-known explanation of this fact was given in 1884 and favoured the acceptance of the dissociation theory in a high degree.

It was to be expected that the opponents of our theory would attack the doctrine of the additive properties. Thus, for instance, Eilhard Wiedemann in 1891 asserted that the replacement of bromine in dissolved potassium bromide through chlorine introduced as gas is the same as the corresponding quantity for any dissolved bromide, *e.g.*, hydrobromic acid. By means of the thermochemical data of Thomsen and Berthelot I showed that the deviations from additivity in Wiedemann's case are about seventy times as great as for the heats of neutralisation.

Another such objection was raised by Kahlenberg, who urged that double decompositions between salts occur not only in aqueous solutions, which are conductors for electricity, thus indicating electrolytic dissociation, but as well in solutions of, *e.g.*, benzene, which were said to be non-conductors. This last assertion was disproved by Allen, Cady, and Lichtenwalter, who investigated the reactions indicated by Kahlenberg more accurately. (Compare N. Dhar, *Zeit. Electrochem.*, 1916, xxii., 275; *Midd. Nobel Inst.*, 1916, iii., 15).

3. *The Diffusion of Electrolytes.*—A property of great theoretical importance is diffusibility. Nernst showed that the diffusion constant of a salt may be calculated as the quotient between the moving force, which here is the osmotic pressure, and the sum of the frictional resistance of its ions, which was calculated by Kohlrausch from the electric conductivity of the salt's solutions. In this manner I determined, for instance, the diffusion constant for 1.7 normal HCl at 12° to be 2.09, in agreement with Nernst's calculation. The constant increased on addition of chlorides such as NaCl, KCl, or NH_4Cl , and thus increase is easily understood if we suppose that HCl as well as the salts is dissociated. If HCl is alone in the water, each H-ion is followed by a Cl-ion; otherwise strong electric charges would appear, and cause forces producing this equality. The diffusion constant is, as said, 2.09 at 12°, whereas if the H-ion moved independently its diffusion constant would be 6.17, and if the Cl-ion moved freely its diffusion constant would reach only the value 1.26 according to the figures of Kohlrausch. If NH_4Cl is added to the water in which the diffusion takes place, the H-ion moves more freely than when HCl is alone, for the positive charge of the diffusing H-ion may be compensated not only by means of the negative charge of a Cl-ion moving together with the H-ion, but also through the positive charge of an NH_4 ion moving in the opposite direction. I found that in 2/N H_4Cl the diffusion constant of the H-ion in 1.04/N HCl reaches the value 4.50, *i.e.*, more than double the diffusion constant in water. The said change is characteristic for electrolytes, and agrees very well with an approximative calcula-

* A contribution to a General Discussion on "The Present Position of the Theory of Ionisation," held at the Faraday Society, January 21, 1919.

tion. On the other hand, the diffusion constant of the chlorine ion in the NH_4Cl solution becomes smaller than 2.09. If the added quantity of NH_4Cl were very much greater than the HCl present, the values 6.17 for the H^+ -ion and 1.26 for the Cl^- -ion would be reached. This observation cannot be explained if we suppose that H^+ and Cl^- are bound to each other. It may therefore be regarded as an *experimentum crucis* for the electrolytic dissociation theory. (Compare Arrhenius, *Zeit. Phys. Chem.*, 1892, x., 74).

4. *Colours of Solutions.*—A very interesting and much discussed additive property is the colour of solutions of electrolytes. At very high dilutions, at which the degree of dissociation $\alpha = 1$, i.e., salts are completely dissociated, the colour of the solution is composed of the colour of the solvent, that of the cation and that of the anion. With an uncoloured solvent, as water, and the one ion uncoloured, all solutions of the salts with a common coloured ion, e.g., all permanganates, ought to have the same colour. This Ostwald showed to be the case (*Zeit. Phys. Chem.*, 1892, ix., 579). He extended this theorem to indicators, in which case the acid or the basis is very little dissociated and gives a wholly different colour from that of its salts. This circumstance was for a time regarded as a strong proof in favour of the electrolytic dissociation. But Hantzsch has made it probable that here a case of isomerism occurs. Opinion then turned over to the other side. It was, for instance, said that we might expect that a concentrated solution of blue vitriol changed colour on dilution because its degree of dissociation increased in a very high degree, and the undissociated salt ought not to possess the same colour as the copper ion. In reality the change of colour is insensible. A very detailed examination of this circumstance was carried out by Robert Wright (*Journ. Chem. Soc.*, 1913, ciii., 528; 1914, civ., 669). He found that strong (nearly totally dissociated) acids exert the same absorptive power on light as their salts, whereas weak (little dissociated) acids often show a great difference in this respect from their salts. This is just what we ought to expect from the view-point of our theory.

5. *The Electric Conductivity of Solutions.*—The first germs of the electrolytic dissociation theory are found in my doctor thesis of 1884. There I conclude that the electrolytes consist of conducting and non-conducting molecules in such an equilibrium that in extreme dilution all molecules become conducting and with increasing concentration the non-conducting molecules increase on the coat of the conducting ones. In this manner the increase of the molecular conductivity with increasing dilution was explained. Later (1887), this theory was proved so that the conducting molecules are dissociated into their ions. Hence the degree of dissociation, α , is calculated by means of the formula—

$$\alpha = \frac{\lambda^v}{\lambda_\infty}$$

in which λ^v is the molecular conductivity for the dilution v (1 grm.-molecule in v litres) and λ_∞ the same quantity for infinita dilution. λ_∞ is a limiting value which may be calculated with the aid of extrapolation formulas given by Kohlrausch and others. This calculation of α was generally accepted and is still regarded as giving nearly reliable results (compare Krauss, *Journ. Amer. Chem. Soc.*, 1914, xxxvi., 61). It is also generally accepted that for higher concentrations a correction for viscosity should be introduced. Mostly it is supposed that this correction is proportional to the viscosity, so that we should introduce $\lambda\eta\eta_m$ instead of λ^v , where η_m is the viscosity of the solution with the dilution v and η_∞ is the viscosity of pure water (at the temperature of investigation). For dilute solutions ($v > 10$) the said correction is for common salts, acids, and bases rather insignificant.

6. *Ostwald's Law.*—Now Ostwald, and at the same time van 't Hoff and Planck, tried to see if the law of Guldberg and Waage for chemical equilibria were not valid for the equilibrium between the dissociated molecules (i.e.,

the ions) and the undissociated ones. Van 't Hoff and Planck, who calculated the figures of Kohlrausch for salts and strong acids and bases, found no agreement between the theoretical demands of Guldberg and Waage's law and experience. Ostwald thereupon calculated some figures of his own regarding weak acids and found good agreement with the demands of the theory, and so he formulated "Ostwald's law" for weak electrolytes (1883). Bredig, a little later, stated that this law holds good also for weak bases. I drew the attention of van 't Hoff to the circumstance that weak acids offered a much better material than salts for investigating the validity of the laws of mass action in the case of electrolytic dissociation, whereupon he, together with Reicher, made a very careful examination of the behaviour of formic, acetic, butyric, monochloroacetic, benzoic, and shimic acids within very wide limits of concentration, and found a wonderful agreement with the law of mass action (1888).

This agreement was rightly regarded as the most convincing proof of the validity of the dissociation theory. But still strong electrolytes made a very marked exception from the said law, and this exception has been one of the most difficult questions in this branch of science. Noyes (1892) rejected the method of determining the degree of dissociation, α , by means of the conductivity, and used for this purpose experiments on solubility of salts (see § 1 above), and supposed that the law of mass action was absolutely exact for this case. As I showed immediately afterwards (1892), the values of α determined in this manner are subject to precisely similar disagreements in regard to the law of mass action as the α -values calculated from the figures of conductivity. These latter have also been generally accepted as being nearly exact for dilute solutions. Some authors, as v. Steinmeyer (1901), Liebenow (1902), Malmatium (1905), Kjellin (1910), and B. Hertz (1912), have tried to explain the deviations from the law of mass action as due to the electrical forces between the charged ions. These authors have been led to different results, and have not taken into consideration that some weak acids obey Ostwald's law even in such concentrated solutions that they contain a greater number of ions per unit volume than solutions of strong electrolytes which show strong deviations from the same law.

7. *Non-aqueous Solutions.*—With solutions in other solvents than water, the deviations from Ostwald's law are often very much more pronounced than for aqueous solutions. It even happens that the electrical conductivity increases more rapidly than in proportion to the concentration of the dissolved salt, which seems to indicate that the degree of dissociation decreases with increasing dilution. This appears to be absolutely untenable from the point of view of the mass action law. (This never occurs with aqueous solutions, if the conductivity is corrected for the viscosity—compare Sloan, *Journ. Amer. Chem. Soc.*, 1910, xxxii., 946). Walden explained it as due to a dissociating influence of the salt molecules, depending upon their high dielectric constant, compared with that of the solvent. He has corroborated his opinion through a great number of measurements.

This dissociating action of the salt may be represented by the formula—

$$\frac{(ca)^2}{c(1-a)} = K + k(ca)^m$$

in which c is the concentration of the salt, K , k , and m three constants. The dissociation constant increases proportionally to the ninth power of the concentration of the ions—here for simplicity only two ions are supposed. For weak acids in water k is very small, so that it may be neglected, and Ostwald's law holds good. For strong acids or bases and for salts K may, except for extremely high dilutions, be omitted. We then get the formula of Rudolphi, or, if $n = \frac{1}{2}$, of van 't Hoff, which fits rather well with observation. Krauss and Bray have proved the validity of their formula for strong electrolytes dissolved in 26 different solvents.

8. *Ostwald's Law for Salt Solutions in Water.*—Kraus and Bray did not find the above formula applicable to aqueous solutions, which have been investigated in very dilute solutions by Kohlrausch and Maltby. This seemed to me very peculiar. I therefore re-examined these figures, which had been found through application of a correction for the conductivity of the water about as great as the conductivity of the dissolved salt itself. The conducting substance in water was indicated as dissolved carbonic acid from the air. Evidently an examination must be carried out, if the correction was right. This was possible by means of an older investigation regarding the equilibrium between any number of electrolytes in aqueous solution (*Zeit. Phys. Chem.*, 1888, ii., 296, and 1890, v., 1) and James Walker's determinations of the conductivity of carbonic acid in aqueous solution (*Journal Chemical Society*, 1900, lxxvii., 5). The result was that the correction to be applied to Kohlrausch's and Maltby's figures never reached more than 0.08 per cent and falls wholly within the errors of observation. In the interval between the concentrations 10^{-5} and $2 \cdot 10^{-4}$ Ostwald's law is valid for NaNO_3 and NaCl with a value of $K=0.024$ (at 18°C). The other four salts (KCl , LiCl , KNO_3 , and LiNO_3) examined by Kohlrausch and Maltby in the same memoir possess nearly the same value of K (*Medd. Nob. Inst.*, 1913, iii., 42).

In a quite recent memoir (*Journ. Amer. Chem. Soc.*, 1918, xl., 131) Weiland has determined the conductivity of potassium chloride, KCl , in extreme dilutions, with the highest possible care and "ultra-pure" conductivity water. He found the constant $K=0.02$, i.e., within the unavoidable errors equal to the value deduced by myself from Kohlrausch's and Maltby's figures. The law of Ostwald is valid at concentrations below 10^{-4} . Sixteen other univalent salts treated by Noyes and Falk give the same value $K=0.02$ in the same interval (Washburn, *Journ. Amer. Chem. Soc.*, 1918, xl., 155).

9. *The Freezing-point of Aqueous Solutions.*—In 1885 Raoult showed that the freezing-point is an additive property changing from 2.0 for univalent negative ions, e.g., Cl , NO_3 , &c., to 0.8 for bi- or poly-valent positive ions, such as Ca , Ba , Al , &c. There are many exceptions; e.g., weak acids, as HCN , CH_3COOH , give only about half the normal value. In 1887 I calculated all figures of Raoult under the assumption that the molecule depression of the freezing-point is 1.85, as demanded by the theory of van 't Hoff, for all kinds of molecules or ions. The agreement was very satisfactory, and thereby a very strong support was given to the electrolytic dissociation theory. Some figures of Raoult were not concordant with the theoretical demands; these cases were re-examined by myself in 1888 and the exceptions found to depend upon errors of observation. The theoretical demands are completely fulfilled in extremely dilute solutions. For more concentrated solutions the deviations may reach considerable values, especially for substances which are known to have a great affinity for water, such as LiCl , MgCl_2 , CaCl_2 , &c. A thorough examination by Noyes and Falk (*Journ. Amer. Chem. Soc.*, 1912, xxxiv., 455) gave the result that for solutions that are not more concentrated than 0.1 normal the difference between the observed figures and those calculated from the electric conductivities does not reach more than 2 per cent for electrolytes consisting of two univalent ions. The same is true for potassium sulphate and lead nitrate. Hygroscopic salts with divalent positive ions show much greater deviations, the lowering of the freezing-point being greater than the calculation demands.

10. *Deviations in Concentrated Solutions.*—In general the lowering of the freezing-point is greater in concentrated solutions than the theoretical value. Exception marks solution of copper sulphate, zinc sulphate, cadmium iodide, and similar salts in which double or complex molecules have been proved to exist. Some authors, as Bjerrum, have therefore expressed the opinion that such electrolytes as KCl are wholly dissociated in solution, and

that the observed deviations from the theoretical value are due to electric attraction between the ions (*Fysisk Tidsskrift*, 1927, xv., No. 2). Milner has calculated the said effect of the electric charges, and Bjerrum finds it agree rather well with the observations for KCl . According to Adams's measurements (*Journ. Amer. Chem. Soc.*, 1915, xxxvii., 495), which are in best accordance with those of Bedford and Jahn, the observed freezing-point of dilute solutions (up to 0.1 normal) of KCl agree with the values calculated from the conductivity within 0.0001°C . Hence the idea of Bjerrum that the electrolytic dissociation of KCl and other salts is complete seems not to agree very well with experience. Much more peculiar is the hypothesis forwarded by Snethlage that the salts, and in general strong electrolytes, should not be dissociated at all (*Zeit. Phys. Chem.*, 1913, lxxxv., 211), which has aroused a great deal of discussion.

It should be remembered that in higher concentrations the values of the molecular conductivity and of the molecular lowering of the freezing-point are dependent upon the unit in which the concentration is expressed. Thus, for instance, the great deviations from van 't Hoff's law for the molecular lowering of the freezing-point for cane sugar, which occur if the concentration is expressed in gm.-molecules per litre, nearly wholly disappear if the calculation is based on molar concentration. The still remaining disagreement may be explained by the rather probable hypothesis that each molecule of sugar binds five molecules of water. (Compare Fraser and Myrick, *Journ. Amer. Chem. Soc.*, 1916, xxxviii., 1907.) Through the investigations of Washburn and others it is very probable that the ions bind rather great quantities of water, which must be taken into consideration when molar concentrations are used, which seem to give the best results. Here rather much work remains to be done before a clear idea can be formed regarding the exact magnitude of the deviations at higher concentrations.

11. *Velocity of Reaction.*—As early as in 1884 it was pointed out that those acids are the strongest which are dissociated in the highest degree. Ostwald showed that the catalytic action of different acids in hydrolysing cane sugar or ethyl acetate is nearly proportional to their electric conductivities. In 1889 I examined this question nearer, and found that the catalytic activity was proportional to the quantity of H -ions present, and further, that foreign substances, specially electrolytes, but also other substances, exerted an accelerating influence on the catalytic process; in this case the inversion of cane sugar was observed. This influence is so great that an addition of a neutral salt not only diminishes the velocity of reaction of a strong acid, which we might expect as a consequence of the diminution of the degree of dissociation of the catalysing acid through the presence of the salt, but even increases it. Most authors therefore suppose that the undissociated molecules of strong acids such as HCl react more rapidly than their H -ions. If the problem is regarded in this manner, it is found that the quotient of the activity of the undissociated molecule to that of the H -ion is the greater the higher the dissociation constant of the acid, so that for weak acids the activity of the undissociated molecule may be neglected.

There is also another method of explaining the action of foreign substances. The velocity of reaction is proportional to the osmotic pressure of the reacting substance. In the case of inversion of cane sugar, the pressure of the H -ion and that of the cane sugar come into consideration. Now, it is well-known that the freezing-point of an aqueous solution containing sugar and a salt is lower than the sum of the freezing-points of the sugar alone and of the salt alone in the same volume of water. The same is the case with a solution of ethyl acetate and salt (Riacte, *Medd. Nobel Inst.*, 1911, ii., 9). Hence, also, the osmotic pressure of the mixture is greater than the sum of the osmotic pressures of its components. The difficulty is to say how much the osmotic pressure of each component has increased. In one case, this is possible, namely, for

the osmotic pressure of H-ions from 0.1N HCl in the presence of different quantities of KCl (Harned, *Fourth. Amer. Chem. Soc.*, 1915, xxxvii., 2460). That this action may suffice for the explanation of the action of neutral substances I have tried to prove on the observations published hitherto (Arrhenius and Andersson, *Medd. Nobel Inst.*, 1917, iii., 25).

The dissociation of weak acids decreases very much through addition of their salts. This causes a proportionate diminishing of their velocity of reaction, in full agreement with theory. On the other hand, the addition of salts of strong acids (such as HCl) increases the velocity of reaction of weak acids. This effect is also provided by theory (Arrhenius, *Zeit. Phys. Chem.*, 1890, v., 1). The degree of dissociation of indicators becomes also increased in a high degree through the addition of neutral salts.

Goldschmidt and Thueren (*Zeit. Phys. Chem.*, 1913, lxxxi., 30) have investigated the velocity of reaction at the formation of esters through the action of organic acids on methyl alcohol in which they are dissolved. This action goes on very slowly, but is accelerated by addition of stronger acids, such as HCl or picric acid. They found that the velocity is nearly proportional to the concentration of the hydrochloric acid and not to the number of H-ions present. At the experiments with picric acid the addition of a picric (0.15N to 0.1N picric acid) does not diminish the velocity of reaction in such a high degree as might be expected—1.6 instead of the theoretical value 1.11. The authors are thereby carried to the conclusion that the undissociated parts of the acids play an important rôle as catalysers—Sneath used this material for his deductions (see Sec. 10). For the weaker trichlorbutyric acid the agreement with the theoretical values is very satisfactory.

These circumstances remind rather much of those occurring in aqueous solutions, and the deviations from the theoretical values seem to be of the same order of magnitude in both cases. The unknown factors are not so well known for the alcoholic solutions as for the aqueous ones. We therefore want still more experience before strict conclusions can be drawn. On the whole, it may be said that the dissociation theory corresponds as well with experience as may be expected in the present state of our knowledge.

KIMBERLEY DIAMONDS: ESPECIALLY CLEAVAGE DIAMONDS.*

By J. R. SUTTON, M.A., Sc.D., F.R.S.S.A.

(Concluded from p. 58).

14. Diamonds in the Matrix.

BAUER tells us (p. 192) that different portions of one and the same broken diamond are never found lying close together in the matrix. He should have said that he had not heard of such a case. As a matter of fact a shattered diamond, mixed up with garnet and olivine, was extracted from its kimberlite matrix in the De Beers sorting office a few years ago. Furthermore, on two or three occasions it has happened that a diamond has been pieced together from its fragments found in the same wash, proving either that it had been broken in the machinery, or that the same fragments had come from somewhere close together in the pipe. And no doubt other fragments could be so pieced together if the sorters had nothing better to do than look for them. For another thing the finds of broken diamonds in the matrix have not been over many, much too few indeed to formulate general conclusions upon. Of the hundred or so specimens of diamond in the matrix which have reached the sorting

office, the majority have been whole diamonds. More specimens could have been procured, no doubt, had they been sought for, especially in the hard blue ground lumps mined from the deeper levels of the De Beers or the Kimberley Mines; but a diamond in the matrix takes some finding, and a searcher might have to turn over many tons of rock before setting eyes on a diamond. At any rate, twenty is a liberal estimate of the number of broken diamonds found in their matrices that have been available for investigation; and there is no earthly reason why in some of these twenty cases we might not have found corresponding fragments of the diamonds could we have found corresponding halves of the matrices. Speaking of matrices, a fine lump of kimberlite, in dimensions about five inches long by four thick, picked up some years ago, contained two well formed diamonds, one a large yellow, the other a small brown one.

15. Yellow Diamonds.

A word must be said about yellow diamonds. From the representative assortments of Pool and Dutoitspan diamonds, given near the beginning of this paper, we get the following comparisons:—

	Pool. Per cent.	Dutoitspan. Per cent.
All stones	19.24	24.96
All cleavages	38.98	41.71
Rejection chips, rubbish, and bort ..	41.77	33.21

Thus there are twice as many cleavages as stones in the Pool, and about one and three-quarter times as many cleavages as stones in the Dutoitspan. Of these, yellow diamonds alone (including off-colours) are—

	Pool. Per cent.	Dutoitspan. Per cent.
Yellow stones	7.68	8.66
Yellow cleavages	11.04	9.93

and leaving out brown and "fancy" (which are largely brown) diamonds, which are—

	Pool. Per cent.	Dutoitspan. Per cent.
Fancy stones	—	3.01
Brown cleavages	5.79	7.88

we have left, of faintly tinted diamonds, whether spotted or not—

	Pool. Per cent.	Dutoitspan. Per cent.
Stones other than brown or yellow ..	11.56	13.29
Cleavages other than brown or yellow	22.15	23.90

That is, the ratio of yellow cleavages to yellow stones is less than the corresponding ratios of brown or of colourless diamonds. It must have been on the basis of some such results as these that Bauer thought he had discovered that coloured diamonds resist fracture better than white ones. Pool information was probably all he had at his disposal at the time.

The significance of the above Pool and Dutoitspan statistics is to be gathered from the fact that foreign orystal inclusions in yellow diamonds are scarce. It is rare indeed for a yellow diamond to come in with a garnet or other mineral embedded in a broken face; and still more for such a mineral to be seen inside a whole stone. With regard to the latter contingency, however, it must be admitted that it would not always be easy to see an inclusion through the common sulcate faces of a yellow stone, though the former is evidence enough that foreign inclusions cannot be frequent. Again, South West African diamonds are often yellow, and the percentage of cleavages to stones is not great among them. An irregular yellow diamond, with grey corners, in my possession contains a garnet in a broken face. A piece of the garnet has been broken away exposing an excellent surface of attachment on the diamond. Spaces in the cavity between the

* From the *Transactions of the Royal Society of South Africa* vii., Part I.

diamond and the garnet are filled up here and there, as usual, with an opaque white substance.

The impression one gathers by way of inference from all these particulars, as well as from a scrutiny of the produce of the various mines round about Kimberley, is that nearly every yellow stone was formed rapidly in one piece out of a single bubble of liquid carbon (stained with iron oxide), or out of a bubble of some solvent containing carbon, thus excluding foreign solids; whereas the Wesselson or the Bultfontein octahedron was built up more slowly, step by step, and layer by layer, thus incorporating foreign solids in the diamond mass. Naturally, a small, loose, foreign, solid body in a cavity larger than itself, occupied by a carbon bubble, would lie at the bottom of the hole if its specific gravity were greater than that of the bubble, or at the top if its specific gravity were less, and in either case need not be imprisoned in the final diamond crystal, though it might stick to a natural face of it. In the case of a diamond crystal continuing to grow by accretion of matter from adjacent carbon bubbles, the foreign solid might be imprisoned in the crystal, but not otherwise. Now clearly there would be more chance of this accretion in magmas where the bubbles were smaller and more numerous—as must have been the case for certain in the Wesselson and Bultfontein Mines—than in magmas where the bubbles were larger and much further apart, as at Dutoitspan. In other words, assuming that diamonds can grow if they get suitable opportunities; they got plenty of opportunities in Wesselson and Bultfontein, but not many in Dutoitspan. Thus, on this view, there is a relativity between—

- (a) The numerous accretionary structures;
- (b) The frequent foreign inclusions;
- (c) The numerous and small diamonds, of such a mine as Wesselson; and
- (a') The few accretionary structures;
- (b') The rare foreign inclusions;
- (c') The fewer and larger diamonds, of such a mine as Dutoitspan.

And this view is confirmed to my mind by such casual inspection as I have been able to make of diamonds won from mines situated outside the Kimberley district. In particular we may say that where diamonds are few or many in number, in any mine, there accretionary structures will be rare or numerous respectively. Wesselson diamonds are singularly accretionary.

How far apart from one another Kimberley diamonds *in situ* are may be illustrated by some examples. From May 16 to June 5, 1917, eighteen working days, 129,640 loads, 2,074,240 cubic feet, of Dutoitspan blue ground were washed, yielding 20,957 carats of diamonds of all sizes, of which a first count gave 40,800 tiny diamonds averaging 78 to the carat (and only worth a penny a piece!), and 36,600 larger ones, of which one was of 126 carats and another of 174 carats; 77,400 diamonds in all, or one to every 27 cubic feet of broken blue ground, equivalent to one diamond to every 17 cubic feet of solid ground before mining. A similar count for Bultfontein showed 174,300 tiny diamonds and 207,900 larger ones, 382,200 in all, in 940,390 cubic feet of solid ground, or 1,504,624 cubic feet of broken ground, *i.e.*, one diamond to every 2½ cubic feet solid, or to every 4 cubic feet loose. Corresponding Wesselson results are 210,000 tiny diamonds and 232,000 larger ones, 442,000 in all, in 1,717,730 cubic feet of solid ground, or 2,748,368 cubic feet of broken ground, *i.e.*, one diamond to every 4 feet solid or to every 6½ feet loose.

Before passing to other matters, it is worth while to suggest that the prevalent rounded form of yellow diamonds is not due, as has been suggested, to attrition or abrasion—the sulcate surfaces of these is suggestive of anything but that—but to the temperature at which they were crystallised and the influence of the colouring matter they contained. ("Rounded edges and other surface irregularities may, however, result from the corrosion of

a crystal subsequent to its growth"—L. J. Spencer, Art. "Crystallography" in "Ency. Brit.," 11th ed., 1910). Surface abrasion is only shown to perfection on diamonds won from alluvial gravels). Some such reason may account for the Pool or the Dutoitspan macles. A remote analogue is the fact that it is the presence or absence of magnesia which has determined whether the red crystal of the Burma ruby mines was to be the regular spinel or the rhombohedral ruby—remote, because in this case the magnesia is an important constituent of the spinel. A closer analogy is the prevailing prismatic habit of the (red) ruby as compared with the pyramidal (blue) sapphire; also aquamarine and emerald crystalline in somewhat different habits. On the other hand, variations in composition do not much affect the habits of garnet and tourmaline. Speaking at large, it may be said that among Kimberley diamonds form depends to a great extent upon colour. Thus, octahedra tend to be colourless; yellow diamonds are mostly rounded; bright yellow macles are decidedly uncommon, even in mines where yellow diamonds abound; ordinary grey bort, when it is symmetrical, is generally in cubes and spheres.

16. Diamond Enclosures.

Just as foreign crystal inclusions are found in diamonds, so diamonds are found embedded in foreign crystals. It is the garnet that is chiefly seen associated with the diamond in this way. All Kimberley garnets are rolled or broken pieces, scarcely ever, if at all, possessing natural crystal faces. Generally also, though not invariably, the embedded diamond shows signs of wear and tear, proving that it must have had a history before the garnet formed upon it. Since, then, garnets are found in diamonds and diamonds in garnets, it follows that both must have originated in the same era of geological time and have crystallised under similar conditions.

Crystal diamonds and bort are also found related to each other in a similar way.

17. Yield.

The following table, taken from the last Annual Report of the De Beers Company, is interesting. It shows the yield in carats per hundred loads of Wesselson and Bultfontein blue—

Table showing the Yield of Diamonds for Wesselson and Bultfontein.

For the 12 months ending June 30.	Wesselson. Carats.	Bultfontein. Carats.
1898	27	—
1899	30	—
1900	30	—
1901	30	—
1902	30	21
1903	30	24
1904	28	29
1905	28	41
1906	28	36
1907	32	34
1908	27	32
1909	34	38
1910	32	37
1911	27	38
1912	29	41
1913	27	42
1914	28	38
1915	26	35
1916	26	40

If the diamond content of the pipes be assumed constant at all depths, we should expect that better methods of extraction with progress of time, to give better yields. Since there are no signs of a better yield at Wesselson, the conclusion ought to be that the ground there gets slightly poorer with depth. At Bultfontein there would seem to have been an improvement with depth. At the

latter mine there is a rough sort of correlation, accidental or not, between the yield and the quality of the diamonds given by it which may be expressed thus—When the yield of carats per hundred loads increases, the percentage of inferior diamonds tends to decrease; in other words, the diamonds are of the best quality where they are packed closest together. When Nature had an abundance of material she used it well in the interests of the market! This is for any given mine; it does not apply comparing one mine with another. For instance, Bultfontein has a higher yield than Dutoitspan, but not such good diamonds. Bultfontein blue ground is somewhat patchy; Wesselton, though poorer, is more uniform.

The De Beers and Kimberley yields are published together as one. Annual values are given in the following table:—

Table showing the Yield of Pool Diamonds.

For the 12 months ending June 30.	Carats.
1892	92
1893	105
1894	89
1895	85
1896	91
1897	92
1898	80
1899	71
1900	67
1901	76
1902	76
1903	61
1904	54
1905	46
1906	41
1907	37
1908	37
1909	42
1910	38
1911	28
1912	31
1913	29

Prior to the amalgamation of the various small companies working the De Beers and Kimberley Mines, the yield was considerably over 100 carats per 100 loads. Not only that, but many of the smaller diamonds used to be thrown away in the rough and ready methods of winning, leaving great heaps of tailings and *débris* well worth washing again in later years. Thus it would seem that the greatest wealth of these two mines was concentrated in the upper levels. On the other hand, only the richer areas were worked to any great extent in the earlier years, the poorer areas being left to spoil the averages of later times.

The Dutoitspan yield for the four years 1911-14 averaged about 22 carats per 100 loads.

18. Anomalous Behaviour of Diamonds on the Grease Tables.

Diamonds appear to have a curious affinity for lime. It was discovered some years ago that diamonds from the Wesselton yellow ground were not readily caught on the grease separators, while it was exceptional for a diamond from the blue ground to fail to be caught. Experiments showed that yellow ground diamonds cleaned in acid lost their non-adhesive property and behaved normally on the tables like blue ground diamonds, whereas blue ground diamonds immersed for a few days in a paste of soft magnesium limestone, or of yellow ground, or in water that had been shaken up with lime or with yellow ground and dried, would not stick to the grease. Evidently the diamonds had acquired a thin coating of lime, which when wetted, lessened the surface tension between them and the grease, and so caused them to behave like the ordinary gravel of the heavy pulsator deposit. Yellow

ground, by the way, contains a large admixture of lime, some specimens losing a good half of their weight after treatment with aqua regia.

It is curious that diamonds left in the blue ground on the depositing floors for a number of years stick to the grease-tables less readily than those which are fresher from the mine. Some Bultfontein diamonds recently washed have this peculiarity. It is not unlikely that they have acquired a fine coating of lime from the soft limestone of the depositing floors.

19. Electrical Conductivity.

True bort, and especially stewartite, is a good conductor of electricity. The regularly crystallised diamond is not, as is sometimes asserted, always a bad conductor. It is a bad conductor if its quality and texture be good, but if it be not highly transparent its electrical conductivity may be nearly as high as that of bort. Wesselton black bort, for instance, which is regularly crystallised, though mostly in fragments, has a conductivity intermediate between transparent diamond and true bort. Some semi-transparent diamonds, greens and browns, are almost as good conductors as Wesselton bort. Further, the conductivity will pretty often have different values along different directions of the same stone. As a rule, the better the quality the lower the conductivity, one exception being that shot bort, though a worse conductor than ordinary grey bort, is a better than Wesselton black bort. We may arrange diamonds in order of conductivity, from the lowest to the highest, somewhat as followz:—

- Fine transparent diamond.
- Inferior transparent diamond.
- Semi-transparent or translucent diamond.
- Wesselton black bort.
- Shot bort.
- Ordinary grey bort.
- Framesite (Transvaal black bort),
- Stewartite.

It would appear from this that impurities have as much to do with the electrical conductivity of diamonds as the habit has.

20. Relative Values.

The relative average values of diamonds exceeding about 0.08 carat each in weight, from each mine, are approximately—

Dutoitspan		100
De Beers		86
Kimberley		76
Wesselton		68
Bultfontein		51

Addenda.

1. On the term "*Macule*" (see § 1).—According to English and French dictionaries, the word is generally said to be French and to be derived from Latin *macula*=a spot. Now it is true that most macles of diamonds are spotted; but so are many well-shaped octahedra. Spots, indeed, are not by any means characteristic of macles, nor the most prominent feature. What is characteristic and prominent in macles is their shape and structure, so well expressed by the Dutch name "*naadsteen*" (seam-stone). There is another French macle, namely, the water chestnut (*Trapa natans*), and in this case the origin of the word has not been traced. Was d'Isle thinking of the latter when he named the former?

2. A Variation in the Size of Wesselton Diamonds, Depth of Working (see § 2).—It is curious that superimposed upon the irregular fluctuations of average size taking place from year to year, their appears to have been a definite increase in the average size of large Wesselton diamonds, i.e., in those of 10 carats or more each. Also it takes a smaller yield now to produce a large diamond than it used to; and the ratio of the weight of large

diamonds to the total yield has increased. This is best shown in a summary, e.g.,

Year.	Average size of large diamonds.	One large diamond in	Ratio of total weight of large diamonds to total yield.
1898-1906	15.6 carats	769 carats	2.0 per cent
1907-1907	15.8 "	731 "	2.2 "

3. *Cubes and Spheres* (see § 6).—Cubes of translucent and of opaque bort are fairly common in Bultfontein, and of semi-translucent bort in Wesselsfontein. Cubes of transparent diamonds also occur, though rarely. The edges of the cubes are always much rounded. The indentations of the surfaces of some cubes tend to a square outline, giving an impression that the mass is built up of a multitude of tiny cubes, whereas the indentations of the surfaces of octahedra are mostly equilateral triangles in plan. Many cubes, as well as octahedra, are pitted with round holes (*cf.* § 12). An existing small yellow cube of transparent diamond shows internal strain. Spheres of translucent bort are called shot bort. Apparently the crystalline aggregates in these incline to a radical arrangement about a central nucleus, which in most cases revealed by cleavage, if not all, consists of a discrete core of diamond or bort.

THE MANUFACTURE OF CHLORAMINE-T.*

By J. K. H. INGLIS.

ALTHOUGH two years have elapsed since Dakin showed the value of chloramine-T as an antiseptic, no detailed account of the method of manufacture has yet been published. The drug has shown itself of great value in cases of cerebrospinal meningitis, diphtheria, &c., and after a trial of a small specimen which I had made, I was asked to supervise the manufacture of a regular supply for the military camps in New Zealand, it having been found impossible to procure it outside the Dominion.

In Dakin's work the starting point for the preparation was *p*-toluenesulphonic chloride, obtained as a by-product in the manufacture of saccharin. No such material being available in New Zealand, details had to be worked out for the manufacture from toluene itself, and these details form the material for this paper.

Sulphonation—The sulphonation of toluene with concentrated sulphuric acid leads to the formation of the three possible monosulphonic acids; but the higher the temperature the larger the proportion of *p*-acid (*Ber.*, 1911, 2504), the highest proportion being 70 to 80 per cent. The price of sulphuric acid being relatively high in New Zealand, I found it best to use two parts by weight of sulphuric acid (sp. gr. 1.84) to one part of toluene (approximately equal volumes) and to carry out the sulphonation at the boiling-point of toluene. 250 cc. of sulphuric acid (1.84) is heated to 110° C. by immersing the reaction flask in a heated paraffin bath, and then 250 cc. of hot toluene is added, the whole being very vigorously stirred with a glass circulating stirrer. The efficiency of the stirring is very important, as upon it depends the time necessary to complete the sulphonation. This reaction was carried out in a flask fitted with a reflux condenser, and only a small loss of toluene vapour took place, sulphonation being complete in about thirty minutes with very little charring. Under these conditions about 75 per cent of the toluene is converted into the *p*-sulphonic acid, the remainder being a mixture of *o*- and *m*-acids. If this mixture of acids was isolated, converted into dry sodium salts, and treated with phosphorous pentachloride, the *p*-chloride could be obtained; but as the other chlorides would be useless there would be a considerable waste of material. We therefore make use of Lange's discovery

(*Ger. Pat.* 57,391) that if water is added so that the mother liquid consists of only 66 per cent sulphuric acid, then on cooling, the crystals that separate consist only of the *para*-acid which separates almost completely—the mother liquid retaining the *o*- and *m*-isomers in solution. In order to carry this out, 45 cc. of water is added to the reaction mixture after sulphonation as above and the liquid poured out and cooled. The liquid rapidly crystallises and sets to a crystalline cake, and on filtering over an asbestos mat (as in a Gooch crucible) nearly the whole of the mother liquid can be drained away, leaving a white crystalline mass, which proves to contain only small amounts of *o*- and *m*-impurities. The crystals that separate appear to be the monohydrate, $C_7H_7SO_3H \cdot H_2O$, and correspond to about 75 per cent of the toluene taken. Hence about 25 per cent of the toluene is either lost as vapour or is contained in the mother liquor in the form of the *o*- and *m*-acids. The separation by crystallisation is, however, not very sharp, and the mother liquid on standing continually deposits further crops, which, however, are nearly free from the *para*-acid.

The *o*- and *m*-acids being useless to us, experiments were made by Mr. C. L. Carter at my suggestion, to see how completely the toluene could be recovered by the action of superheated steam. It was found that if the liquor were heated to about 170° and then a brisk current of steam at 200° were blown through it the bulk of the toluene was rapidly evolved, the distillate containing at first as much as 20 per cent toluene. When the percentage fell below 5 per cent the operation was stopped, as further continuance was hardly profitable (*Armstrong, Journ. Chem. Soc.*, 1884, xlv., 148). The total amount thus recovered was about 14 per cent, leaving 11 per cent not account for. Part of this is lost by evaporation during mixing and subsequent sulphonation, and a small part is left in the sulphuric acid. Probably most of the remainder is lost by evaporation *in vacuo* during the filtration of the crude acid.

The cake of crude *p*-acid is dissolved in water, slightly more than enough calcium carbonate is added to precipitate the sulphuric acid as calcium sulphate, and the still acid liquid is filtrated. It is then nearly neutralised with caustic soda, made distinctly alkaline with sodium carbonate, boiled, and again filtered. It is important to remove the calcium as completely as possible, as it may become a troublesome impurity in the later stages. This method gives a solution containing only sodium sulphate and sodium carbonate, and on acidifying with hydrochloric acid and evaporating to dryness there remains a pure white salt consisting of the required sodium sulphate with a trace of sodium chloride. The sulphate is so soluble in water that this seems to be the best method of preparation.

Preparation of the Sulphonic Chloride.—This can easily be prepared by heating together on the water bath approximately equal weights of sodium salt (dried at 140° C.) (191 gm.) and phosphorous pentachloride (208.5 gm.). In this case the reaction takes place very rapidly and easily and a large amount of phosphorous oxychloride is obtained. Mr. C. S. Hicks, working in my laboratory, found, however, that the oxychloride itself can be used according to the equation $2XSO_3Na + POCl_3 = 2XSO_2Cl + NaPO_3 + NaCl$, and he obtained a 76 per cent yield. Hence if less than half the weight of pentachloride be taken and the mixture be heated some hours on the water-bath under reflux condenser the following reaction takes place— $3XSO_3Na + PCl_5 = 3XSO_2Cl + 2NaCl + NaPO_3$. The proportions of salt and pentachloride according to this equation are 573 to 208.5, or 2 3/4 to 1; but the reaction is very slow towards the end as the mass becomes too solid and the yield is apt to decrease. This trouble might be avoided by using the theoretical proportion of pentachloride and sufficient oxychloride, which should then be recovered unchanged. An experimental trial of this gave 92 per cent yield, but the oxychloride was not recoverable. We therefore used 2 parts of sodium salt for each

* From the *Journal of the Society of Chemical Industry*, September, 1918.

part of pentachloride, and the action then completes itself more easily, and only small amounts of oxychloride are left over—the reaction being allowed to go on over night under reflux condenser on a water-bath. The oxychloride is then distilled off *in vacuo* and the residue put into cold water. The sulphonic chloride is the only part insoluble, and is separated by filtration; a small amount of oily impurity (*o*- and *m*-sulphonic chlorides) can be pressed out from the solid cake. The yield is nearly quantitative, 95–99 per cent. The solid sulphonic chloride still contains small amounts of *o*- and *m*-impurities, but these are gradually eliminated in the later stages.

(To be continued).

THE CONFIGURATIONS OF ORGANIC COMPOUNDS AND THEIR RELATION TO CHEMICAL AND PHYSICAL PROPERTIES.*

By ARTHUR MICHAEL.

(Continued from p. 55).

Catalysis.—This phenomenon depends on the formation of a "polymolecule" of the organic substance and the catalyte (Michael, *Am. Chem. Journ.*, 1908, xxxix., 3; *Ann.*, 1912, cccxc., 43), when the added free energy in the system enables the increase of entropy, accompanying the transmutation of a maleinoid into a fumaroid derivative, to take the place at a lower temperature, or when it is already proceeding, with acceleration of velocity. This hypothesis, which offers the only known explanation of the relations between the quantity of the catalytic reagent and the course of the reaction (Michael, *Am. Chem. Journ.*, 1908, xxxix., 4), and also the effect of energy in *status nascens* (*Ibid.*, 5) (56), has been already applied to explain a number of stereomeric reactions (*loc. cit.*, pp. 4–14).

In this paper another problem, the catalytic behaviour of bromine in stereomeric rearrangements, will be considered, as in this field untenable conclusions have been drawn from apparently paradoxical facts. Van't Hoff's observation ("Dix Années dans l'Histoire Théorie, 1887, 99), that maleic acid in concentrated aqueous solution gives at once in sunlight and with a trace of bromine a precipitate of fumaric acid, was continued by J. Wislicenus ("Verh. Saech. Gesell. zu Leipzig," 1895, p. 489) (57), who was able in this way to stereomutate up to 93.5 per cent, and who extended the method to allocrotonic and angelic acids. Wislicenus also found that tiglic dibromide is partially converted into angelic dibromide, and this fact, with the observed limitation in the conversion of maleic acid, led him to conclude that the reactions are reversible; *i.e.*, that the fumaroid acids are partially catalytically convertible into the maleinoid stereoisomers.

Fittig (*Ann.*, 1898, ccciv., 117) showed that citraconic acid in solution and in the dark is not stereomerised but adds bromine slowly, while in the sunlight up to 68 per cent of mesaconic acid is formed, and also concluded that the catalytic reaction is reversible. He apparently supported the view by proving that dimethyl fumaric acid is transformed in chloroform solution by traces of the halogen to the extent of about 90 per cent into the maleinoid acid, which then decomposes into anhydride and water.

Wislicenus assumed *cis*-addition to angelic and tiglic acids, and accordingly grouped the dibromides with the mother substances, but we now know that *trans*-addition takes place, and a comparison of the configurations of the dibromides shows that a reversion in the energy relations has occurred (*Journ. Am. Chem. Soc.*, 1918, xl., 715). The conversion of the maleinoid tiglic dibromide into the fumaroid angelic derivative is therefore not anomalous.

With the symmetrical introduction of two methyl groups into maleic (K_1 , 1170×10^{-5}) and fumaric (K_1 , 90×10^{-5}) acids, changes in the relative energy relations occur which bring those of the new acids much nearer together than they are even in citraconic (K_1 , 340×10^{-5}) and mesaconic (K_1 , 70×10^{-5}) acids (*loc. cit.* 719). This means that the stereomutation of dimethyl fumaric acid requires much less energy than that of fumaric acid; but the final product in the conversion is dimethylmaleic anhydride, which is formed spontaneously from the acid; *i.e.*, with loss of free energy, and which may be the factor which determines that the change, dimethyl fumaric acid $\rightarrow$ dimethyl maleic anhydride plus water, proceeds with a decrease of free energy. Evidently this reaction cannot be considered an illustration of a catalytic transformation proceeding with an increase of free energy in the newly formed substance.

That the subject of catalysis and of balanced reactions in organic chemistry is in such confusion is largely due to the improbable theoretical conceptions with which it has been burdened by the physical chemist. It begins with the definition that catalysis is due to the presence of certain substances which accelerate the velocity of reactions already proceeding in their absence (58). The free energy in any mechanical or chemical system must be able to overcome the hindrance to a change, which is otherwise not conceivable. To assume, as is done in the often-quoted typical illustration, because hydrogen and oxygen may be united catalytically, or at a high temperature, the union is proceeding at all temperatures above absolute zero is certainly not scientific.

Again, it is stated that a catalyte cannot influence the "affinity of a process," an unfortunate phrase, as a process does not show an affinity, and that its "action does not extend to the motive force of a reaction, but to overcome the hindrance to the progress." The latter indefinite assumption is contrary to the function of catalytes acting chemically which depends on the formation of "polymolecules," whose motive forces thereby become greater. Such a relation, however, does not contradict the second law of thermodynamics, since in the final phase of the reaction the catalyte is present without any change in its energy content.

Furthermore, the statement that a "catalyte does not take part in the reaction" is open to criticism as being ambiguous, and the further statement that a catalyte must "invariably change the velocity of the reaction in a reverse direction," is by no means beyond doubt. The latter assumption is closely connected with the physico-chemical explanation of the cause of balanced reactions, but in the only organic reaction that has been thoroughly examined experimentally, *i.e.*, $\text{iso-C}_4\text{H}_9\text{Br} \rightleftharpoons \text{tert-C}_4\text{H}_9\text{Br}$, this explanation has been proven to be untenable (Michael and collaborators, *Ann.*, 1910, cccclxxix., 286; 1912, cccxcii., 92; *Journ. Am. Chem. Soc.*, 1916, xxxviii., 654; compare Brunel, *Ann.*, 1911, cccclxxxiv., 245; *Journ. Am. Chem. Soc.*, 1917, xxxix., 1978) (59).

This brings us back to the assumptions of Wislicenus and Fittig, that bromine does not catalytically convert the maleinoid ethylenic acids into the fumaroid forms completely, because the reactions are reversible. A chemical reaction is always feasible under ordinary conditions if there is a possibility of an increase of entropy, which itself depends on physical as well as on chemical changes; in fact, on the sum total of all the involved energy changes (*Journ. Am. Chem. Soc.*, 1910, xxxviii., 654, footnote 4). To convert fumaric acid into maleic acid would require a considerable expenditure of energy, which in the above case could have only been obtained from the solvent, but as maleic acid is much more soluble in water such an endothermic reaction is extremely improbable. From any point of view fumaric acid should be formed in theoretical amount barring the small quantity of dibromide that is formed at the same time (Wislicenus, "Verh. Saech. Gesell. zu Leipzig," 1895, p. 489), if it were completely insoluble in the surrounding media, and

* From the *Journal of the American Chemical Society*, xl., No. 11.

the insolubility factor undoubtedly dominates in the extent of this stereomutation. Indeed, it may be the means of transforming a fumaroid into a maleinoid derivative catalytically; e.g., mesaconic acid is much more soluble in ether than citraconic acid, and if its "polymolecule" with bromine should have sufficient energy to overcome the hindrance to stereomerisation the maleinoid acid would be formed to an extent depending on the insolubility factor. (An investigation of this subject with the use of different solvents and also with the products kept in solution would be of great theoretical interest).

Esterification (60).—The direct process in the crotonic acid series was examined by Michael and Oechslein (*Ber.*, 1910, xlii., 322), and no general relationship could be traced between the velocity and the affinity constants; butyric acid showed a much greater velocity than either of the stronger crotonic acids. Later, Thomas and Sudborough (*Journ. Chem. Soc.*, 1912, ci., 317) proved that this relation holds between other saturated and ethylenic α,β -unsaturated acids, and deduced the following rules from their experimental results:—I. Where the difference in the strength of the acids is not very marked the unsaturated α,β -acid is esterified less readily, although it is "slightly stronger," and II. unsaturated β,γ -acids are esterified more readily than the corresponding saturated acids. Rule I. is based in part on a comparison of the affinity constants of acids with dissimilar configurations; thus, the value of (trans) cinnamic acid (3.5×10^{-5}) is compared with that of (cis) hydrocinnamic acid (2.3×10^{-5}), and the true analogue, allocinnamic acid (1.4×10^{-5}), is decidedly stronger. Indeed, it is more than doubtful if a general connection exists between the affinity constants and the esterification velocities of these acids, although in respect to the latter values the following rule appears to be valid:—The cis- and trans-forms of ethylenic α,β -acids and their α - and β monochloric-derivatives are esterified less readily than the corresponding saturated acids. Rule II. was deduced from the behaviour of trans- β,γ -acids, and as no data for the corresponding cis-derivatives is at hand it should be restricted to trans-compounds.

The rules show conclusively that in direct esterification the determining factor cannot be, as supposed by Stewart ("Stereochemistry," p. 321), the "strength of the acid," as the stronger (61) unsaturated trans- α,β -acids under I. show much smaller velocities, while the likewise stronger trans- β,γ -acids under II. show larger values than the corresponding saturated derivatives. Thomas and Sudborough's results also prove that in isomeric trans-acids unsaturation in the α,β -position has a much greater retarding effect than in the β,γ -place, which is opposite to their influence on the affinity constants.

In direct esterification the writer (*Ber.*, 1908, xlii., 312) assumed the primary formation of a "polymolecule" of acid and alcohol; then in accordance with Henry (*Ber.*, 1877, x., 2041) that of the additive product $R-C(OR)(OH)_2$, which decomposes into ester and water. According to this view the velocity depends primarily on the relative quantity of the free energy in the carbonyl of the acidic group, and on the affinity relations of its carbon and oxygen to the alcohol addendum. If the effect of a chemical change is to increase all these factors then an acceleration necessarily follows; otherwise the change depends on a resultant which cannot be foreseen with certainty.

The transition from propionic to acrylic acid removes $\overset{3}{H} + \overset{4}{H}$ and $\overset{4}{H} + \overset{5}{H}$ from the $\overset{1}{C}$ and $\overset{1}{O}$ of the carbonyl, which increases the free energy in that group, and also the affinity of the oxygen to the alcoholic hydrogen of the addendum, but decreases that of the carbon to the $C_nH_{2n+1}O-$ group to a greater extent, as the influence of $\overset{3}{H}$ is greater than $\overset{5}{H}$, and carbon is chemically the more "plastic" element (Michael, *Journ. Am. Chem. Soc.*, 1910, xxxii., 993). Since the resultant of these forces is decidedly negative we should expect the same

relation between other pairs of similar saturated and unsaturated acids (Rule I.).

The change from acrylic to crotonic acid introduces $\overset{4}{CH_3}$ and $\overset{5}{CH_3}$ as positive groups in the trans-positions to the $\overset{1}{C}$ and $\overset{1}{O}$, which cause a decrease in its free energy, and a proportionately greater decrease in the affinity of the carbon than increase of that of the oxygen to the addendum. These are the same affinity relations as before, and the velocity should decrease.

A further fall in the velocity takes place with the substitution of the cis-H in crotonic acid (1.4 per cent) by $\overset{4}{CH_3}$; i.e., dimethylacrylic acid (0.6 per cent), because it introduces the positive $\overset{4}{CH_3}$ to the carbon and $\overset{5}{CH_3}$ to the oxygen of the carbonyl, and for the same reason the value for trans- α,β -pentenic acid (0.8 per cent) is less than that of crotonic acid. The shifting of double linkage from the α,β - to the β,γ -position brings the positively acting $\overset{2}{CH_2} + \overset{3}{CH_2}$ to the $\overset{1}{CO}$, in place of the negative influence $\overset{2}{CH} + \overset{3}{CH}$, and is accompanied by a large velocity increase (Rule II.). Thomas and Sudborough (*Journ. Chem. Soc.*, 1912, ci., 317) also found that the values of the saturated normal valeric acid (13 per cent) and β -phenylpropionic acid (18.2 per cent) are less than those of the β,γ -unsaturated ethylidene propionic (22.6 per cent) and benzylidene propionic (39.4 per cent) acids; and they give the rule that β,γ -unsaturation increases the velocity. This conclusion is too broad and should be

restricted to trans- β,γ -acids. In this change $\overset{4}{H} + \overset{5}{H}$ to the carbon and $\overset{5}{H} + \overset{6}{H}$ to the oxygen of the carbonyl are eliminated, and theoretically the velocity should decrease but to a much smaller extent than with a α,β -unsaturation.

According to these chemists if the α,β,Δ -acids are very much more acidic than the corresponding saturated derivatives the velocity relations are reversed, and the first acids are easier esterified. This conclusion appears to have been based on a comparison of the acid methyl maleate (21.8 per cent) and the acid methyl succinate (11.3 per cent), but the true stereo analogue is the acid methyl fumarate (Bruni, *Atti Accad. Lincei*, 1904, [5], xiii., 1., 626), whose affinity constant should be less than that of the acid maleate, and whose esterification velocity may not be as great as that of the acid succinate. The great increase in the reaction velocity of the maleate is due to a carbon and the oxygens of the carbomethoxyl group being in the 5 and 6 cis-positions to the carbonyl of the carboxyl, which greatly increases its free energy and additive capacity for the alcohol.

Notes.

56. Here chemical explanations of Skraup's observations are given (*Monatsh.*, 1891, xii., 133–141). There is no theoretical or experimental foundation for this chemist's view that catalysis is directly contingent on secondary chemical processes; on the contrary, facts are known that disprove it; nor does his "chemical resonance" throw any light on the subject. It is merely an improbable suggestion.

57. Wislicenus overlooked van't Hoff's earlier observations.

58. Nernst, "Theoretische Chemie," 1917, p. 574. The following definitions are taken from this book, as it is usually considered authoritative on physical-chemical subjects.

59. The writer believes that the relations disclosed in his investigations on this subject are not uncommon in reversible organic reactions.

60. Many of the conclusions given by Werner in his "Lehrbuch der Stereochemie" (pp. 377–400) on this subject are untenable, as the different relations to struc-

ture shown in direct and catalytic esterification were not taken into consideration.

61. In the hexyl series the relations are reversed (*Journ. Am. Chem. Soc.*, 1918, xl., 719).

(To be continued.)

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, January 23, 1919.

Sir J. J. THOMSON, O.M., President, in the Chair.

THE following papers were read:—

"Experiments Demonstrating an Electrical Effect in Vibrating Metals." By Admiral Sir HENRY JACKSON, G.C.B., F.R.S., and G. B. BRYAN, D.Sc.

Experiments are described which demonstrate the electrical effect produced by vibration in wires and other metallic bodies, and a means of detecting and recording them by means of searching coils connected to delicate recording apparatus.

The diminution of the effect when the surface of a steel wire is rusted is dealt with, in continuation of a paper by one of the authors on the subject of vibrating wires.

The inductive effect of a vibrating wire on a neighbouring circuit is mentioned, and that this led up to the fact that all metallic bodies experimented with, whatever their shape or material, generate eddy currents, which can be detected in them by using suitable searching coils.

That this effect is primarily due to the vibrating conductor cutting the lines of the Earth's magnetic field is proved by the experiments; but that there seems to be a residual effect, not at present fully accounted for, which is greater than can be attributed to experimental errors.

Details of the tests are described. These have been carried out with wire bridges, tubes, utensils of various forms and materials, and also with Chladni plates. The circulation of the currents in the latter seems to follow a fixed law. This may be presumed to be generally applicable.

The elimination of possible errors due to mechanical or air vibration affecting the searching coils is dealt with, and it is shown that these are nearly negligible when the search-coils are of rigid and suitable mechanical construction.

"Wave Resistance: Some Cases of Three-dimensional Fluid Motion." By Prof. T. H. HAVELOCK, F.R.S.

It is shown how to calculate the wave resistance when the surface pressure is two-dimensional, and the wave pattern is like that of ship waves. Certain cases are examined in detail, and the method can be extended to more complex systems. Interpreting some of the results in terms of the related problem of a submerged body, expressions are obtained for the wave resistance of a prolate spheroid and of other bodies.

"Chances of Loss of Merchant Ships." By W. S. ABELL.

This communication discusses the effect of damage to vessels in respect of chances of loss of bulkheads and the consequent chances of loss of vessels. If the extent of damage be fairly constant, as in torpedo explosions, it would appear that there is an inferior limit to spacing of bulkheads. Further, as carriage of cargo is impeded by subdivision, there is economic reason for calculating the number of bulkheads sufficient for reasonable safety. Such calculation involves discussion of chances of loss of one or more bulkheads, and of relation of size of vessel to bulkhead spacing.

Assuming that water-tightness is destroyed within radius R from centre of damage, it is shown that—

- (1) Where bulkhead spacing = $2R + a$, the "odds on" for loss of one bulkhead are $2R/a$;
- (2) Spacing = $2R - a$, odds on for loss of two bulkheads are $a/(2R - 2a)$; and
- (3) Spacing = $R - a$, odds on for loss of three are $2a(R - 3a)$.

These results are applied to the case of ordinary cargo-carrying vessels of fixed type but of varying lengths, with $R = 20$ feet representing longitudinal extent of torpedo damage.

Diagrams accompanying indicate that—

- (1) For a given standard of subdivision, decrease of size of large vessels only slightly increases chances of loss;
- (2) For small vessels, risk of loss is relatively high, and it is doubtful whether any subdivision whatever is effective for vessels below 320 feet length;
- (3) Safety increases markedly with length of vessel;
- (4) Intermediate bulkheads are more useful in larger vessels, but may also, in certain cases, increase risk of loss.

By suitable assumptions the method may be used to discuss subdivision of passenger vessels exposed to ordinary marine risks.

"A Critical Study of Spectral Series. Part V. The Spectra of the Monatomic Gases." By Prof. W. M. HICKS, F.R.S.

This Part V. deals with the serious relationships in the second or blue spectra of the rare gases. Not only are the S, D, and F series allotted, but the discussion serves to amplify and sustain the laws developed in preceding parts, and illustrates their value for the purpose of the analysis of spectra in general. Amongst new methods may be mentioned the use of the links, discovered in Part IV. of these communications, for the purpose of dealing with lines expected from formulæ or other considerations which lie outside the observed region. Thus, in the case of a wave number n of a line in the ultra-violet $n - e$, or $n - u$, or *vice versa* if the ultra-red $n + e$, $n + u$ where e , u are definite and calculable quantities may be wave numbers in the observed region, and correspond to lines actually seen. In this way it is possible to obtain evidence of the existence and wavelength of lines belonging to the spectrum although not actually measured.

Of importance, also, in the general theory of spectra, is the discovery of summation series. Thus in the case of the ordinary well-known series, the wave numbers are represented as the difference of two quantities $A - \phi(m)$ where m is the order in the series. It is shown that in the case of the F series at least there are, in addition to these difference frequencies, also a corresponding series of summation frequencies given by $n = A + \phi(m)$. For S, D series, such series, if existing, would occur far down in the ultra-violet.

The values of the ϕ are determined with very great accuracy, in general to within 1 in 100,000, and thus serve to determine atomic weights to 1 in 7000, or the ratio of atomic weights to 1 in 200,000. The values found are as follows, the values found by chemical methods being appended for comparison.

	Ne.	A.	Kr.
	$\delta 14'4708 \pm .0006$	$57'9209 \pm .0002$	$249'540 \pm .002$
	$W. 20'0005 \pm .0004$	$40'0141 \pm .0006$	$83'0550 \pm .0003$
Chem. W.	20'2	39'88	82'92
	N.	Ra.	Em.
	$\delta 611'0100 \pm .0017$	$1787'021 \pm .05$	
	$W. 129'963 \pm .0008$	$222'259 \pm .003$	
Chem. W.	310'2	222 to 222'4	

CHEMICAL SOCIETY.

Ordinary Meeting, December 19, 1918.

Prof. W. J. POPE, C.B.E., F.R.S., President,
in the Chair.

THE PRESIDENT referred to the loss sustained by the Society, through death, of the following Fellows:—Charles Stewart Maries (died on Service), Douglas Rayment Keller, John Bishop Tingle.

Certificates were read for the first time in favour of Solomon Nathan Brown, 30, St. James' Road, Higher Broughton, Manchester; Harold Frank Cabell, B.Sc., 66, Anson Road, Gretna, Carlisle; Vishwanath Ganesh Dani, B.A., 25, Carlingford Road, Hampstead, N.W. 3; Alfred Farmbrough, 259, Lewisham High Road, S.E. 4; James Darnell Granger, Ph.D., c/o The Chiswick Polish Co., of Australia, Ltd., Mitchell Road, Alexandria, near Sydney, N.S.W.; Walter Arthur Nelson Hardwick, 26, West Kensington Mansions, W. 14; Andre Job, 18, Avenue d'Orleans, Paris, France; Sydney Walter Morris, 46, Braithwaite Road, Sparkbrook, Birmingham; Charles Moureu, 18, Rue Pierre Curie, Paris, France; William Adrian Thomas Nash, 1, St. Barnabas Villas, Guildford Road, S.W. 8; Josslyn Vere Ramsden, c/o Cox and Co., 16, Charing Cross, S.W. 1; Thomas John Samuel, Travellers' Well, Pwll, Llanelly, Carm.; Edward Tyghe Sterne, Trenton, Ontario, Canada.

The following Certificate has been authorised by the Council under By-law I. (13) for presentation to ballot:—Parnell Stanley O'Dowd, 43/2, Canal East Road, Calcutta, India.

Prof. F. SODDY, M.A., F.R.S., then delivered his lecture, entitled "*The Conception of the Chemical Element as enlarged by the Study of Radio-active Change.*"

A vote of thanks to Prof. Soddy for his lecture, proposed by the PRESIDENT and supported by Sir WILLIAM TILDEN, was carried with acclamation.

Ordinary Meeting, January 16, 1919.

Prof. W. J. POPE, C.B.E., F.R.S., President,
in the Chair.

It was announced that the Society had lost, through death, the following Fellows:—Charles William Dick (died on Service), John Ernest Dunstan, William Lamond Howie, Hassum Alidina Lakhani, Thomas Stratford Logan, George Cannon McMurtry, George Frederick Tyler Phillips, William Ping, Richard Spencer, James Carter Spensley.

Messrs. D. R. Ridge, B. Jeffs, J. W. R. Youll, W. H. Tomlinson, and W. D. Haigh were formally admitted as Fellows of the Chemical Society.

Certificates were read for the first time in favour of Walter Richard Berry, B.Sc., 128, High Street, Chorlton-on-Medlock, Manchester; Harry Blackman, 25, Walden Street, New Road, E. 1; Philip Blackman, 33A, Pirnness May Road, Stoke Newington, N. 16; Harold Samuel Bolton, 33, Schubert Road, East Putney, S.W. 15; Alan Charnley Burns, B.Sc. Tech., High Street, Whitehaven; John Arthur Clements, The Quintas, Spital, Chesterfield; Thomas Robert Dixon, Innisfayle, Cyprus Avenue, Bloomfield, Belfast; Percy Edwin Evans, M.A., 86, Chesterton Road, Cambridge; Geoffrey Isherwood Higson, M.Sc., 11, Westbourne Road, Berkdale, Southport, Lancs.; Edward Likiernik, B.Sc., University of London Club, 19, Gower Street, W.C. 1; Francis Falconer Peel, B.Sc., The Bryn, Monkham's Drive, Woodford Green, Essex; Frank Radcliffe, M.B., B.S., 18, Rawlinson Road, Southport; Frank Comer Savage, 44, Elfindale Road, Herne Hill, S.E. 24; Ernest Shepherd, B.Sc., Tollington School, Muswell Hill, N. 10; Arthur John Griffiths Smout, 41, Hazelhurst Road, King's Heath, Birmingham; Rupert Harry Truelove, B.Sc., 65, Hamp-

ton Road, Forest Gate, E. 7; Frederick Wilson Walker, 89, High Street, Welling, Kent; Walter Henry Watson, B.Sc., 19, Lightcliffe Road, Palmers Green, N. 13.

It was announced that on and after January 1, 1919, the hours of opening the Library will be as follows:—Mondays, Wednesdays, and Thursdays, from 10 a.m. to 6 p.m.; Tuesdays and Fridays, from 10 a.m. to 9 p.m.; Saturdays, from 10 a.m. to 5 p.m.; and in the evenings of those days on which the Chemical Society meet. These extended hours of opening have been arranged in connection with the scheme in which a number of kindred societies have joined for the enlargement and increased utility of the Library.

NOTICES OF BOOKS.

The Chemistry of Synthetic Drugs. By PERCY MAY, D.Sc. (Lond.), F.I.C. Second Edition. London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. 1918. Pp. xii+250. Price 10s. 6d. net.

MANY English firms are now engaged in the manufacture of drugs which before 1914 were obtained exclusively from Germany, and investigations dealing with the nature and preparation of drugs are proceeding with considerable vigour in many laboratories, so that a second and enlarged edition of this work will receive a cordial welcome on all sides. The author does not attempt to give detailed accounts of processes of manufacture, but rather discusses the theoretical aspects of the subject, and the book will be specially interesting as suggesting fresh lines of research and extended investigations of new classes of compounds, such as the arsenic and antimony organic derivatives to which a whole chapter is devoted. In the first three chapters the theory of the action of synthetic drugs, the effects of various elements and radicals, and the chemical changes which drugs undergo in the animal body are discussed, an attempt being made to draw some definite conclusions as to the relation between physiological action and chemical constitution. Although some generalisations can be made there are many exceptions and discrepancies which call for further research, and to these the author calls the attention of his readers. The different groups of drugs classified according to their physiological action are considered in turn, and here many additions have been made to the second edition to bring the text up to date. For example, the antiseptics derived from acridine are described and the chloramines also. The author has succeeded in making a highly technical subject very interesting, and the book will be found very stimulating by organic chemists as well as by those interested in the manufacture of synthetic drugs.

Reports of the Progress of Applied Chemistry issued by the Society of Chemical Industry. Volume II., 1917. London: Harrison and Sons, for the Society of Chemical Industry. Pp. 536. Price 6s. 6d.

THESE reports, which are issued at a very moderate price, provide a comprehensive view of the progress which was made during 1917 in all the most important branches of chemical industry, and many classes of workers will find them exceedingly useful. The teacher will welcome them, as enabling him at the minimum expenditure of energy to keep up to date his knowledge of branches other than those in which he has specialised, and the practical man will find that they give him valuable information as to progress in all directions. Finally, the research worker can learn from them exactly what has been achieved and what still remains to be done. The reports deal with all the important branches of chemical industry, and have been written by experts who have special opportunities of acquiring knowledge and estimating the importance of recent developments, and references to current literature

are very complete. In many departments much progress is reported, such as for example in chemical engineering, to which the war gave a considerable impetus, and in the manufacture of fine chemicals, in which branch Germany's pre-eminence has been lost, it is to be hoped for ever. In fact it may be said that in spite of war conditions, on the whole, chemical industry in this country is in a more flourishing condition than five years ago, and its future is more promising, while the output of research, though necessarily restricted to a certain extent, gives no cause for alarm.

MISCELLANEOUS.

Institution of Electrical Engineers.—We have been asked to announce that Prof. Carey Foster is very ill and may pass away at any moment.

Institution of Civil Engineers.—At the meeting held January 29, this Institution elected upon its Roll of Distinguished Honorary Members—Marshal Foch, O.M., Field Marshal Sir Douglas Haig, K.T., Admiral Viscount Jellicoe of Scapa, G.C.B., O.M.

MEETINGS FOR THE WEEK.

MONDAY, 10th.—Royal Society of Arts, 4.30. "Scientific Problems of Electric Wave Telegraphy," by Dr. J. A. Fleming.

TUESDAY, 11th.—Royal Institution, 3. "Study of Electric Arcs and their Applications," by Prof. J. T. MacGregor Morris.

WEDNESDAY, 12th.—Royal Society of Arts, 4.30. "The Government and the Organisation of Scientific Research," by Sir Frank Heath.

THURSDAY, 13th.—Royal Institution, 3. "The Movements of the Earth, Sun, and Moon," by Dr. W. Wilson.

— Ceramic Society, 3. (In co-operation with the English China Manufacturers Association in the Central Schools of Science and Technology, Stoke-on Trent). "Recent Work on the Booc China Body," by Dr. J. W. Mellor.

FRIDAY, 14th.—Royal Institution, 5.30. "Earthquake Waves and the Interior of the Earth," by Prof. C. G. Knott.

SATURDAY, 15th.—Royal Institution, 3. "Bach's Use of the Orchestra in his Works," by Prof. H. P. Allen.

LECTURE ASSISTANT & LABORATORY STEWARD.

Well qualified LECTURE ASSISTANT AND LABORATORY STEWARD required for the CHEMISTRY DEPARTMENT of the Sir John Cass Technical Institute, Jewry Street, Aldgate, London, E.C. 3. Salary £120 to £150 per annum, according to qualifications.—Applications, stating qualifications, to be sent to the PRINCIPAL, by MARCH 1st.

CITY OF CARDIFF EDUCATION COMMITTEE.

THE TECHNICAL COLLEGE.

Principal—CHARLES COLES, B.Sc. (Lond.).

The services of the following Full-time LECTURER are required:—

HEAD OF CHEMISTRY AND APPLIED CHEMISTRY DEPARTMENT (a Specialist in Applied Chemistry). Commencing salary £500 per annum.

Applications on foolscap paper, stating age, full qualifications, teaching and other experience, and giving copies of not more than three testimonials, should reach the PRINCIPAL (from whom further particulars may be obtained) by MARCH 17, 1919.

Relatives of eligible men on War Service are requested to bring this advertisement to their notice.

JOHN J. JACKSON, B.A.,
City Hall, Cardiff. Director of Education.

If in good condition, Sixpence per copy will be paid for any of the undermentioned numbers of the CHEMICAL NEWS which may be forwarded to this office:—

3053, August 2nd, 1918.

3054, August 16th, 1918.

3059, October 25th, 1918.

3063, December 20th, 1918.

16, NEWCASTLE STREET, FARRINGTON STREET, LONDON, E.C. 4

A Discharged Soldier seeks situation as Works

Chemist, or Laboratory Work, practical and theoretical experience. Good testimonials.—Address, D. S., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Analytical and Consulting Chemist, M.Sc.,

A.I.C. (Food and Drugs), will buy existing Practice or purchase Partnership with view to extension.—Address, Box 135, W. H. Smith and Son, Kingsway, London, W.C. 2.

Chemist (25), ex-Army N.C.O. (1915-16),

desires Appointment at home or abroad in Works or Laboratory. Can control labour; good Analyst. Two and a-half years in large Government Factory.—Address, B., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Chemist, with several years' experience,

desires post in Works with a view of obtaining experience in Technical Processes; Oil Fuel or Food preparation preferred. At present on active service in France.—Address, R. E., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Chemist in charge seeks change. Metals,

Minerals, Analyses; Plant control and organisation. Research (Inorganic) and new plant inception specially preferred. Good references and varied experience.—Address, "Organiser," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Ex-Officer, disabled, four years experience of

Analysis, including Foods and Drugs, requires responsible Position.—Address, X. O., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Glass-blowers (Scientific) wanted.—Apply,

Baird and Tatlock, Ltd., 45, Renfrew Street, Glasgow, or 38, Portland Street, Manchester.

Inter. B.Sc. requires post in Chemical Works

or Laboratory, in or near London. Lately demobilised as student.—Address, W. G. B., 7, Livingstone Road, Clapham Junction, S.W. 11.

London Honours Graduate, A.I.C., twenty

years' experience Foodstuffs, General Analysis, and Bacteriology, now supervising Works Laboratory, desires responsible progressive Post where energy and initiative will meet with recognition.—Address, L. H., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Works Analytical Chemist required. One

conversant with Soap Manufacture, Nicotine Extractions, and Agricultural and Horticultural Preparations. State full particulars and salary required.—Address, W. A., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Wanted by large Belgian Vinegar Works,

manufacturing Date Wine and Alcohol Vinegar, a reliable General Agent for England. First-class references indispensable.—Write, 44, Chaussee d'Etterbeek, Brussels, Belgium.

Wanted, Copper-lined Steam jacketted

VACUUM PAN; capacity about 200-300 gallons.—Address, V. P., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

FRANCE (BORDEAUX and SUD-OUEST).—

Representations wanted by French Engineer Chemist of good firms (for Chemical Products, Chemical Machineries, Chemical Apparatus, New Processes).—Address TEYSSIER, 301, Cours Balguerie, Bordeaux.

STAFFORDSHIRE EDUCATION COMMITTEE

ASSISTANT LECTURER IN METALLURGY.

The Staffordshire Education Committee re-

quire an ASSISTANT LECTURER IN METALLURGY for the County Metallurgical and Engineering Institute, Wednesbury.

Applicants should possess a University degree or an equivalent qualification, and be fully competent to take classes in Chemistry, Metallurgy, and Metallography; and it is desirable that they should have had both Teaching and Works experience.

Salary offered £250 to £300 per annum, according to qualifications.

Further particulars and form of application may be obtained from the undersigned, by whom applications must be received on or before MARCH 5th, 1919.

C. F. MOTT,
County Education Offices, Acting Director of Higher Education.
Stafford, January, 1919.

THE CHEMICAL NEWS

VOL. CXVIII., No. 3070.

PHOSPHORITES AND SUPERPHOSPHATES FROM THE POINT OF VIEW OF THE SULPHUR INDUSTRY.

By DR. LOUIS TIRELLI.

THE great progress of new industrial applications, modern conceptions which tend to group around a main industry, subsidiary manufactures which increase its output, the excellent results obtained elsewhere, thanks to the utilisation of the by-products of the principal manufactures, have all brought to light in the sulphur industry the need of utilising in one way or another the enormous quantities of sulphurous acid which are at present lost in the extraction of sulphur from ores by partial combustion.

Given the situation of the mines, the possible variations in the output of sulphur in a given locality and the many variations in the cost of production and sale price of the raw material, the method of utilisation to be sought should fulfil the following conditions:—

1. It should not require costly and unwieldy plant and apparatus.
2. It should be easy and safe to apply, and should be capable of adaptation to simple manufacture which only calls for a plant with few complications.
3. It should furnish a product which can find an immediate, easy, and extensive use.

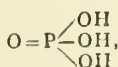
Without stopping now to examine the different processes proposed, tried, or applied in analogous industries for the utilisation of the sulphurous anhydride contained in the furnace gases of various ores, it is worth while to study a method which has raised great hopes, and which is directed towards utilising the gases from sulphur extraction furnaces by combining the sulphurous anhydride which they contain with insoluble mineral phosphates with a view to transforming them into soluble products (superphosphates). This product would thus be obtained in a direct and economical way by the immediate combination of the sulphurous anhydride and the phosphorite without the use of lead chambers, &c., necessary for the manufacture of these substances in fertiliser factories.

It is unnecessary to emphasise the importance of such a practical application by which would be obtained a most useful product, for which the already great demand is continually increasing, while utilising directly the sulphurous gases in a simple and rational manner.

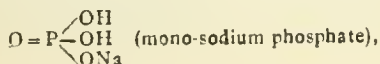
Since this idea presents such an attractive aspect, since it has even formed the subject of recent patents, and as, moreover, from the theoretical point of view there is no *a priori* difficulty of a chemical nature, I venture to think it would be interesting to deal with it briefly, to determine whether it would be capable of application and whether tests with a view to its realisation would justify themselves in the future.

Phosphoric Acid and Pure Phosphates.

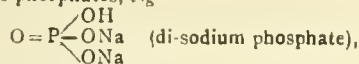
Phosphoric acid is a tri-basic acid formed thus:—



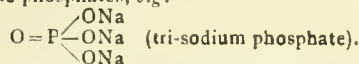
in which, as in all oxyacids, the electro-negative hydrogen atoms of the hydroxyl group may be replaced by metals to form salts. We have thus:—



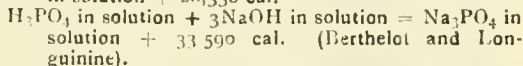
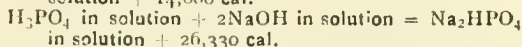
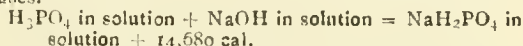
Di-metallic phosphates, e.g.—



Tri-metallic phosphates, e.g.—



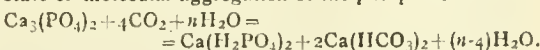
Physico chemical determinations have shown that the three acid functions of phosphoric acid present, in progressive saturation by bases, different degrees of affinity, that it to say the first behaves like that of a strong acid, the second like that of a weak acid, and the third merely like that of a phenol. This is clearly shown, for example, in the determination of the heats of combination with the bases.



It is also shown by the action of the salts on indicators. Thus, while a solution of mono-sodium phosphate is distinctly acid towards litmus and to phenol-phthalein, a solution of di-sodium phosphate is alkaline to litmus and neutral to phenol-phthalein, and a solution of the tri-sodium salt is alkaline to both these indicators.

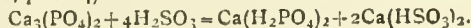
Given this slight acidity of the second and third acid groups of phosphoric acid, it is evident that even a weak acid can displace it from its di- and tri-basic salts by removing a portion of the base with which it is combined, thus causing a state of equilibrium depending on different coefficients (relative affinity of the two acids for the base, concentration, &c.) with which we need not concern ourselves here.

The above mentioned fact is apparent not only in the presence of soluble alkaline salts, but also, for example, in the presence of precipitated tri-calcium phosphate, which is insoluble, or nearly so. If the latter is placed in suspension in water and the water is saturated with carbonic acid, it dissolves fairly well, giving rise to a certain extent to the following reaction, determined quantitatively by the laws of chemical equilibrium, and according to the state of molecular aggregation of the phosphate:—

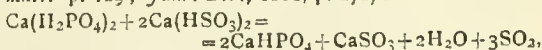


Mono-calcium phosphate. Calcium bi-carbonate.

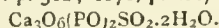
If the tri-calcium phosphate is treated with a dilute mineral acid in excess, even if the latter is weak, the salt dissolves completely, forming soluble mono-calcium phosphate. In the same way, if a solution saturated with sulphurous acid acts on it in excess, mono-calcium phosphate and calcium bi-sulphite are formed and remain in solution (Piltner, *Chem. Ind.*, 1878, p. 393; *Fahr. Ber.*, 1878, p. 1124):



If the solution obtained is boiled the excess of sulphurous acid is set free, the bi-sulphite is decomposed, and a bi-calcium phosphate and neutral sulphite of lime, almost insoluble in water, separate out (Rotondi, *Ann. di Chim.*, lxxiv. p. 129; *Fahr. Ber.*, 1882, p. 272):—



and also hexagonal crystals of the composition (Gerland, *Fahr. Ber.*, 1870. p. 312; 1871, p. 286)—



* There is an appreciable difference between newly precipitated tri-calcium phosphate and the dry salt, which depends on the more or less pronounced state of molecular aggregation. The former is gelatinous and dissolves in water in the proportion of 8 : 100,000; the latter, on the other hand, is a white powder soluble only in the proportion of 3 : 100,000.

It would appear then that the reaction which is produced when the precipitated phosphate is employed should take place in an industrial process in which mineral phosphates are used, under certain conditions, and that it would be possible to transform them into soluble salts by the aid of pure sulphurous acid in place of the solution of sulphuric acid which is employed at present, the manufacture of which necessitates special and costly plant. However, in spite of the fact that theory and scientific experiments made with the pure product in a state of feeble aggregation offer prospects of a possible realisation of the process, it must be admitted that little hope remains when natural products and questions of a practical nature are considered.

Tri-calcium Phosphates and Phosphorites.

The difference which exists between precipitated tri-calcium phosphate and the phosphorites is due essentially to the other products which the latter contain, and to the mineralisation which the tri-calcium phosphate, their principal constituent, has undergone.

Although it is generally stated that the phosphorites consist of amorphous phosphate of lime, it should be pointed out (and this fact is proved by microscopic examination) that a portion has been changed to a complex state of aggregation, even to the extent of producing a crystalline form in variable quantity, actual specific minerals mingled with the mass being thus produced (ornithite, xylite, dahlite, apatite, caxoxene, &c.). This state of aggregation is more or less pronounced according to the nature, quantity, and duration of the action of the agents which have modified the original product (fossilised remains of animals) during different periods and in special conditions of formation. The result is that there is a notable difference between the original substance and the phosphorite, not only as regards form, molecular aggregation, hardness, composition, &c., but also as regards the manner in which they behave in the presence of chemical reagents; this difference resembles from this point of view that which distinguishes precipitated silica from mineralised silica.

Industrial Treatment of Phosphorites.

The transformation of the mineral phosphates into soluble phosphates is carried out ordinarily by means of sulphuric acid, acting upon the finely crushed substance. It is necessary—

(a) That the ore should be mechanically crushed as finely as possible, so as to allow access for the acid, for disaggregation and reaction, to each particle, and to facilitate thus molecular contact of phosphates and acid;

(b) That the acid used should be in sufficient quantity, and of a given concentration (48° 54° Bé.) to suit the greater or less amount of calcium carbonate, earthy and metallic phosphates, fluorides, phosphosilicates, &c., contained in the phosphorites, so that disintegration and reaction with the phosphate occur at a temperature which is such that these actions may be complete, and so that the water present, whilst sufficient for the reaction and for the bodies which are formed, may not form too moist a product;

(c) That the duration of the reaction should be long enough and the mixture homogeneous;

(d) That the superphosphate should not under any circumstances be exposed to a high temperature (90–100°).

If any one of these conditions be not carried out, the process will not be satisfactory, and the manufacturer will suffer losses which may be considerable, for the profits are wiped out if all the phosphoric acid is not transformed.

In industrial practice disintegration and transformation of the phosphorites into soluble salts is carried out in two stages:—

(a) Mechanical pulverisation, as complete as possible.

(b) Action of the quantity of sulphuric acid necessary under the above-mentioned conditions.

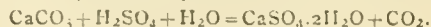
Passing over the mechanical process, we may note that

the action of the sulphuric acid also takes place in two stages:—

(a) Reaction on and disintegration of the mass.

(b) Reaction and molecular disintegration of the phosphate.

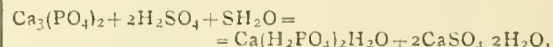
The action of the sulphuric acid on the particles of the phosphorite, which forms a more or less compact agglomerate of phosphates, carbonate of lime, fluorides, silicates, &c., causes first the immediate conversion of the carbonate of lime into hydrated sulphate:—



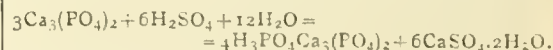
This rapid reaction, which gives rise to considerable heat and sets free an appreciable quantity of gas (CO_2), assists not only the disintegration of the particles of phosphorite, but also the subsequent reactions, which require a certain temperature, and by which the sulphuric acid replaces and sets free hydrofluoric and hydrosilicic acids, &c., which thus assist to a considerable extent in the disintegration of the most refractory compounds. The importance of this reaction between calcium carbonate and sulphuric acid for the success of the operation is clearly shown by practical experience, which proves that phosphorites which contain an insufficient quantity of calcium carbonate disintegrate slowly and with difficulty; they remain "cold," in technical language, and yield a wet product of poor quality. These phosphates require treatment with a warmer and more concentrated sulphuric acid, or (a less satisfactory method) to be mixed as intimately and homogeneously as possible with phosphates rich in lime, such as phosphatic chalks.

The action of sulphuric acid on these secondary compounds assists contact with the phosphate, whilst the carbon dioxide which is set free renders the mass porous, and the heat which is generated increases the power of substitution of the sulphuric acid and assists its action on the compounds of iron and aluminium, phosphosilicates, &c., which are present.

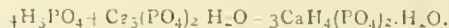
The reaction between the tri-calcium phosphate and the sulphuric acid, which produces soluble phosphate, does not take place as is generally shown—



but also takes place in two distinct stages—in the first, which is instantaneous, free phosphoric acid is formed, and a part of the tri-calcium phosphate remains unattacked,

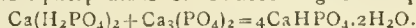


In the second, the reaction is slowly completed, in the presence of excess of water, producing mono-calcium phosphate,



The reaction takes place in two stages not only because sulphuric acid has an affinity for the bases which is double that of phosphoric acid, but above all because phosphate of lime, whilst mechanically broken up, is not in a molecular state, as is for instance a salt in solution; it is composed, on the contrary, of more or less complex molecular aggregates, so that the interior molecules are protected from contact with the acid, whilst the exterior molecules are exposed to the action of an excess of acid which would suffice practically for the conversion of the whole mass. It is to the presence of these aggregates and groups, and to the fact that the penetration of the acid is to some extent hindered, that we must attribute the fact that, even when in practice more acid is used than is strictly necessary for the treatment of the mass, a portion of the phosphoric acid exists in the form of a bi-basic salt, soluble only in citrate. In fact, the molecules which do not come into direct contact with the free acid (sulphuric or phosphoric) can only react with the molecules in which conversion into a mono-calcium salt has taken place, and

bi-calcium phosphate is formed according to the equation,



The phosphates of iron and aluminium, which occur in variable quantity in phosphorites, behave in an analogous fashion, yielding variable quantities of free phosphoric acid, according to the degree of concentration of the sulphuric acid, the temperature, duration of the reaction, &c. As these phosphates are more refractory, the reaction must be as complete as possible, so that no insoluble phosphoric anhydride remains to cause a decrease in percentage solubility.

The phosphosilicates and silicates are attacked partly by the hot sulphuric acid, partly by the hydrofluoric acid, which carries down silica in the form of silicon fluoride, which is subsequently found again in the gas-washing chambers.

Phosphorites and Sulphurous Anhydride.

Having studied, in their successive developments, the principal phenomena which occur between sulphuric acid and phosphorites, and the conditions indispensable to the smooth operation of the process, we can easily understand that it is very difficult in practice advantageously to replace the sulphuric acid by sulphurous anhydride. Were it not so, it would be strange that in so prosperous an industry as that of the superphosphates, such a substitution should never have been contemplated and tried.

It is evident, *a priori*, that the use of liquefied and dry sulphurous anhydride cannot be considered, if only by reason of the fact that in these conditions it has no acid action; we are therefore limited to the use of an aqueous solution of sulphurous anhydride, either ready prepared or produced by the contact of the sulphurous gases with the phosphorites in the presence of water or moisture. It is known that sulphurous acid in solution behaves towards bases like a weak acid and that its salts may be decomposed by weak and dilute acids. The action of soluble salts on indicators shows the weak acid qualities of sulphurous acid. The acid salts (for example, bisulphite of soda, NaHSO_3) are neutral to methyl-orange, while neutral salts (for example, sulphite of soda, Na_2SO_3) are alkaline.

If we admit for a moment that the power of combination of sulphurous acid is equal to that of phosphoric acid (that is to say half as great as that of sulphuric acid) these two acids, when in the presence of a base in insufficient quantities for saturation, will divide it amongst them in direct proportion to their respective concentration, or rather to their mass.

Now whilst phosphoric acid may be mixed with water in any proportion, sulphurous acid forms, above 40° , solutions of variable concentration according to the temperature and pressure, while below 40° the concentration of the solution is below that determined by the pressure according to the law of Henry and Dalton. With pure sulphurous anhydride at 15° and 760 mm., we obtain an aqueous solution containing 43.56 volumes of sulphurous anhydride per volume of solvent, that is to say about 12.4 per cent by weight of sulphurous anhydride. It corresponds from the acidimetric point of view to a solution containing about 19 per cent of sulphurous acid; from the point of view of its avidity of combination with the bases, it is much less active than an equivalent solution of sulphuric acid.

Up to the present we have dealt with sulphurous anhydride of 100 per cent purity. In practice we have to deal with sulphurous gases produced by the combustion of an ore containing sulphur, such as are given off in smelting furnaces; the average richness of this gas in sulphurous anhydride does not exceed 5 to 6 per cent by volume. The solution obtained by the contact of these gases with water, if the sulphurous anhydride obeyed the law of Henry and Dalton at temperatures below 40° , would be of a concentration at 15° and 760 mm. of

$$\frac{43.56 \times 5 \text{ or } 6}{100} = 2.173 \text{ to } 2.613$$

litres per litre of water used, that is to say 0.62 to 0.74 per cent of sulphurous anhydride by weight. Therefore in order to obtain a solution of the same concentration as we obtain with 100 per cent sulphurous anhydride, we should have to exert upon the gases which contain 5 per cent of sulphurous anhydride a pressure greater than 20 atmospheres.

As, on the other hand, the sulphuric acid which the treatment of ordinary phosphorites demands in practice should be of a concentration of 52 to 53° B $\acute{e}$, it is obvious that we are far from the conditions indispensable to the industrial process, even if we assume that there is no specific difference of combination and substitution between the two acids. It is known that in practice the dilution of sulphuric acid to the extent of only one degree Beaum $\acute{e}$ yields an inferior product, and that the strength of sulphuric acid increases within certain limits with the temperature, even with relation to stronger acids (HCl , HNO_3), whilst the strength of sulphurous acid varies inversely with the temperature of the solution.

Let us admit even that when working with high pressures one can obtain a solution of sulphurous anhydride sufficiently concentrated and active to be able to produce the desired effects of disaggregation at molecular disintegration upon the particles of phosphorite; but when the pressure employed is relieved and the excess of water necessary to bring about contact between the sulphurous anhydride and the phosphorite is removed, the removal of the excess sulphurous anhydride and the decomposition of the bisulphite formed will immediately cause the re-conversion of the acid phosphate of lime to bi-calcium phosphate.

Experiments and Experimental Tests.

The industrial conversion of mineral phosphates into soluble phosphates by means of sulphurous anhydride has been attempted repeatedly, and has continually given rise to various patents, of an essentially theoretical nature, taken out by people who are obviously not familiar with the above-mentioned facts.

One of the first patents of this sort was that of the "Pilter" Company (D.R.P. 2661) which did not lead to any practical result. Nor did those which followed it. We remain therefore limited to the use of sulphurous anhydride either simply to enrich in tri-calcium phosphate the phosphatic chalk (Ramsay and Gouthrie, D.R.P. 105,387) by eliminating the excess of carbonate of lime in the form of soluble bisulphite, &c., or to attempt to convert the bone phosphate into soluble products.

If we consider that bones contain phosphate of lime in a non mineralised form, it is natural that after the failure of all attempts to transform the phosphorites the hopes of experimenters should have been directed towards bone phosphates, all the more because the use of liquid sulphurous anhydride as a solvent for fats and oils gave promise of the possibility of using sulphurous anhydride first for the extraction of fats, and afterwards for the extraction of phosphate of lime by means of water or steam; the residue would then only consist of cartilage, ossein, &c.

Dr. Max Schroeder has particularly gone into this interesting question, but his tests have not led to any result, as is shown clearly by the conclusions of a work published at the time of the Chicago Exhibition. (Dr. Max Schroeder, "Die wasserfreie flüssige schweflige Säure und ihre Verwendung in der Industrie," Buchdruckerei Kühne, 1894).

"The extraction of mono-calcium phosphate by means of an aqueous solution of sulphurous acid has frequently been proposed and attempted, without the discovery up to the present of a profitable use. . . ."

"There is no doubt that neither of the two processes mentioned, the extraction of fats from bones by means of liquid sulphurous anhydride under pressure, and the extraction of acid phosphate of lime from bones by

aqueous sulphurous acid, has yet acquired the least practical value.

In conclusion, I give the results obtained from some experiments in treating phosphorites in a divided state with sulphurous acid—

1. (a). *Tennessee Phosphorite*, containing 35.7 per cent of phosphoric anhydride. Samples finely crushed and pressed through gauze. Five grms. were taken and left to digest for twelve hours in 10 cc. of a saturated solution of sulphurous anhydride containing 300 cc. of SO_2 at 20° . The whole was placed in a closed vessel and the water evaporated at $60-70^\circ$, mixed again with 10 cc. of sulphurous solution and left to digest again for twelve hours.

Phosphoric anhydride soluble in water ..	Trace
Phosphoric anhydride soluble in citrate (grms.) ..	0.130
Total phosphoric anhydride soluble (grms.) ..	1.785

Appearance of powder little changed, coloration red-dish as before (sulphuric acid turns it grey).

(b) *Gafsa Phosphorite*, containing about 27—27.1 per cent of P_2O_5 . Treatment as before.

Phosphoric anhydride soluble in water ..	Trace
Phosphoric anhydride soluble in citrate (grms.) ..	0.14
Total phosphoric anhydride soluble (grms.) ..	1.35

Appearance of powder little changed; only that one can determine, by means of the microscope, the presence of sulphite and sulphate of lime which cover the particles here and there.

2. *Tennessee Phosphorite*, pulverised, &c., as before. Fifty grms. of powder were taken, mixed with 50 cc. of water, and a cold and moist current of 100 per cent sulphurous anhydride was passed through for five hours at a pressure of about 1.5 atmospheres.

Phosphoric anhydride soluble in water (per cent) ..	0.32
Phosphoric anhydride soluble in citrate (per cent) ..	2.41
Total phosphoric anhydride soluble (per cent) ..	35.6

Appearance of powder little changed.

3. *Porous Tennessee Phosphorite*, broken to size of 1 to 3 cc., divided into two parts, which were submitted to the following treatments:—

(a) The first was treated with distilled water for two hours.

(b) The second was treated with a saturated solution of nitrate of soda for two hours.

Afterwards it was placed in a tube and exposed for eight hours to a cold moist current of 100 per cent sulphurous anhydride.

Analysis showed:—

(a) Phosphoric anhydride soluble in water and citrate (per cent) ..	1.25
(b) Phosphoric anhydride soluble in water and citrate (per cent) ..	1.62

The treatment with a solution of NaNO_3 was intended to increase the action of the sulphurous anhydride on the phosphate by an oxidising action; the increase of solubility observed in the second case is due in all probability to the formation of a sodium phosphate by double decomposition between the calcium salt and the nitrate.

In other experiments, the powder has been exposed in thin layers to the long-continued action of a current of moist sulphurous anhydride, cold at $60-70^\circ$, of 100 per cent purity, and diluted to 50 per cent, but with no better results.

In a general way it may be said, from the results of chemical determinations and microscopic observations, that sulphurous anhydride only reacts at the surface of the particles of phosphorite, producing especially the bibasic salt, and that this is the limit of the action.

It is known that porous substances assist the combination of sulphurous anhydride with oxygen, and it might be thought that by choosing certain very porous phosphorites and submitting them at a suitable temperature to the action of a strong current of oxygenated sulphurous gas, one would encourage thus the formation of sulphurous anhydride in the mass, so as to bring about the desired reaction and disaggregation, either directly owing to the humidity of the gases or by a subsequent addition of water.

Without stopping to consider the reactions which would take place at high temperatures, if the phosphate could react under these conditions, let us note the results of the following experiment:—

Some very porous fragments of phosphorite were submitted for about ten days at $400-450^\circ$ to a current of gas containing about 20 per cent of SO_2 and 9 per cent of oxygen by volume and traces of moisture.

The fragments of phosphorite from 1—5 cm. thick which were submitted to this treatment and left for some days in a damp atmosphere became covered on the surface with a light grey powder, damp and uniform, while the lower and internal layers hardly appeared to be changed; nothing more than a light white efflorescence of hydrated sulphate of lime could be observed. Analysis showed—

(a) Superficial powder with acid reaction, damp appearance, and grey coloration—

Humidity at $60-70^\circ$ (per cent) ..	6.2
Phosphoric anhydride soluble in water (per cent) ..	8.9
Phosphoric anhydride soluble in citrate (per cent) ..	1.7
Insoluble phosphoric anhydride (per cent) ..	7.5

(b) The internal portion of the fragments of a brownish-red colour, when reduced to an impalpable powder, contained—

Phosphoric anhydride soluble in water (per cent) ..	0.1
Phosphoric anhydride soluble in citrate (per cent) ..	1.5
Insoluble phosphoric anhydride (per cent) ..	32.6

Other samples submitted to analogous treatment gave similar results. Hence it is clearly evident that one cannot reckon on an eventual conversion of sulphurous anhydride into sulphuric anhydride by the action of porous phosphorites in the presence of oxygen. If such an action is produced it is limited to the surface, as occurs when oxide of calcium is used. It is therefore useless to examine the considerable and numerous difficulties which would offer themselves to the practical realisation of this process, which has no chance of success.

Summary.—To summarise the considerations and facts brought forward, we are obliged to reject any possibility of the practical utility of proposals, patents, &c., directed towards this end, which offer *a priori* some prospects of success. The question which is of most interest, that is the utilisation of the sulphurous anhydride which escapes from sulphur smelting furnaces (corresponding to a quarter or more of the sulphur obtained) still remains, and can only be solved when it is decided to proceed, with more enterprise and initiative, with the necessary experiments, with a view to setting on foot the progress and developments by which this industry is certainly capable of benefiting.—*La Revue des Produits Chimiques*, xxii., No. 1.

The Sir John Cass Technical Institute.—A distribution of prizes and certificates by Charles C. Carpenter, Esq., D.Sc., Chairman of the South Metropolitan Gas Company, will take place on Tuesday, February 18, 1919. The chair will be taken at 8 p.m. by Sir Thomas H. Elliott, Bart., K.C.B., Chairman of the Governing Body.

THE MANUFACTURE OF CHLORAMINE-T.*

By J. K. H. INGLIS.

(Concluded from p. 58).

Preparation of Sulphonamide.—This operation, though quite simple in theory, causes a certain amount of trouble without special apparatus. The alternative methods are treatment with ammonium carbonate on the water-bath and treatment with strong ammonia solution. The latter method, if properly controlled, is decidedly the more satisfactory. If the sulphonic chloride is ground to a fine powder and concentrated ammonia is poured upon it, a violent reaction begins almost at once and the liquid boils. In this way considerable amounts of ammonia are driven off, and the action is apt to be incomplete. We had some difficulty in procuring vessels in which the reaction could be conveniently carried out under pressure, and owing to the impossibility of getting special vessels made which would stand the action of the hot mixture of ammonia and ammonium chloride, we used stoneware ginger-beer bottles which had a screw stopper with a rubber seating. 100 gm. of sulphonic chloride could be placed in each, 100 cc. of 0.880 ammonia quickly added, and the stopper screwed in firmly. On shaking vigorously the action began, and as soon as the bottle became too hot to hold it was placed in cold water. No mishaps occurred, and the yield was excellent, the liquid only requiring filtering and the residue washing with cold water. The mother liquors on evaporation give small amounts of the *m*-amide but very little else besides the ammonium chloride. Under these conditions about half the ammonia taken is actually used, and on a large scale the unchanged ammonia could be recovered by boiling the liquors. The yield of *para*-sulphonamide is 94–97 per cent.

Preparation of Chloramine-T.—The conditions for the conversion of amide to chloramine were given in detail by Dakin, one mol. of amide being dissolved in 1.2 mols. of sodium hypochlorite of definite concentration, and the chloramine then precipitated by the addition of strong brine. At first his actual proportions were used, but it was found to be unnecessary to use brine. If the amide is dissolved in a warm, strongly alkaline solution of sodium hypochlorite of concentration 1.3 to 2.0 N, a large crop of chloramine is formed on cooling and the remainder can easily be obtained on evaporation. It is very important to have a decided excess of caustic soda, and for each mol. of amide we usually take 1.05 to 1.1 mols. of hypochlorite and 1 mol. of sodium hydroxide. The preparation of the hypochlorite is of course straightforward. Owing, however, to the cost of acids in New Zealand and to there being no electrolytic source of chlorine, we found it most convenient and cheapest to use bleaching powder as the starting point. The crude chloramine-T obtained in this way is contaminated with sodium chloride; but even the crude crystals on drying contain 92–95 per cent of chloramine. The substance can be easily purified by recrystallisation from water. If dissolved in twice its weight of hot water, a large proportion can be obtained in the pure form (over 98 per cent) on cooling. The final filtration is apt to be troublesome; the crystals do not pack well on the filter and it is therefore difficult to remove the mother liquid completely. If, however, the cooling is carried out rapidly without stirring, a different shape of crystals is obtained which filters much more readily. It is thus possible, working with large quantities, to get a product of over 99 per cent purity.

Utilisation of By-products.—In the sulphonation as described most of the toluene is used, but half the sulphuric acid taken is contained in the mother liquors after removal of the toluene by superheated steam. At first it was hoped that it would be possible to recover the acid in

the pure state by distillation and use it over again; but there is always some charring and the impurities remaining make it comparatively useless. It contains 34 per cent of water. In the remaining stages of preparing the sulphamate the by-products are small in quantity and comparatively valueless. Some lime or calcium carbonate is used and converted into sulphate, but the quantity is very small. In the preparation of the sulphonic chloride the by-products are sodium chloride and sodium *ortho*- and *meta*-phosphate. It would probably be worth while to utilise the latter on the large scale, but our experiments are incomplete. In the preparation of the sulphonamide the chief by-products are ammonium chloride and excess of ammonia. The former can be easily recovered and the ammonia could be made use of with suitable apparatus.

In the preparation of hypochlorite and of chloramine, the by-products are calcium carbonate—a nearly pure precipitate—and a liquor consisting of sodium chloride and hydroxide. No doubt use could be made of this liquor, but we have made no attempt in this direction. The above results have been obtained under laboratory conditions making some pounds of chloramine per week. Owing to lack of filtering apparatus and other labour-saving devices we have not made experiments on a still larger scale; but our experiments have always been made with a view to their application to large-scale operations, and we have every reason to believe that they would not fail in commercial practice.

THE CONFIGURATIONS OF ORGANIC COMPOUNDS AND THEIR RELATION TO CHEMICAL AND PHYSICAL PROPERTIES.*

By ARTHUR MICHAEL.

(Concluded from p. 70).

In catalytic esterification a primary product of mineral acid catalyst and alcohol (62) has been assumed, which unites with organic acid to form a still larger "polymolecule," and the next phase may be similar to that in the direct process. Owing to the strong negative character which the general acid catalyst gives the "polymolecule," it seemed more in line with chemical analogy to assume that, like the "polymolecule" of hydrochloric acid and an alcohol, it decomposes with the substitution of the alcoholic hydroxyl by the acyl radical into catalyst, ester, and water (Michael, *Ber.*, 1909, xlii, 311) (63).

Thomas and Sudborough (*Journ. Chem. Soc.*, 1912, ci., 318) have objected to the above interpretations, and state "our own view is that the direct and catalytic esterification are essentially the same, the only difference being that in the former case the organic acid is its own catalyst." This old and widely accepted but indefinite view is not proven, nor does it offer an explanation of the mechanism of the process. In the direct method the organic acid is its own catalyst if more than one of its molecules and the alcohol unite to form a "polymolecule," which should then change chemically according to the above-mentioned Henry hypothesis. The purpose of such a gathering of acid molecules would be to overcome the hindrance in the addendum to the addition; i.e., to aid the separation of the hydroxyl hydrogen of the alcohol by the resulting accumulation of the free energy in the system. In the esterification of acetic acid, which even in a vapour state consists largely of "polymolecules," this may occur, but this view cannot in a general sense be considered probable, although in some other cases direct esterification may proceed in such a manner.

The velocity in catalytic esterification appears to depend primarily on the affinity of the "polymolecule" of the

* From the *Journal of the Society of Chemical Industry*, September, 1918.

* From the *Journal of the American Chemical Society*, xl, No. 11.

mineral acid catalyst and alcohol to the acid, as expressed in the sum total of the free negative energy in the carboxyl group, and should be, owing to the strong negative character of the "polymolecule," inversely proportional to the negative value of that acidic group (Michael, *Ber.*, 1909, xliii., 312). That this carboxyl value does not necessarily coincide with the affinity constant of the respective acid is seen in the relations of the velocity values to the affinity constants in stereoisomers of the type $RHC=CRCOOH$. Owing to the direct union of CH_2 to $COOH$ in ethylenic β,γ -acids, and the less intimate relation of the acidic group to the Δ -carbons than in α,β -acids it agrees with the above view that the members of the first group of monobasic acids show greater velocity values than their isomers in the latter class. Anomalous, however, is the more rapid esterification of trans- β,γ -acids than the corresponding saturated derivatives, but this may be due to the comparison of acids with unlike stereostructures.

Sudborough and Roberts found that in substituted acrylic acids the " β -compounds are, as a rule, esterified more readily than the α -isomeric" (*Journ. Chem. Soc.*, 1905, lxxxvii., 1842), and later, Sudborough and Davies state that "a comparison of the values for tiglic and dimethyl acrylic acid at once shows that these acids are exceptional" (*Ibid.*, 1909, xcv., 977). The rule applies, however, in all known cases if it is restricted to trans- β -compounds.

Tiglic and dimethylacrylic acids do not constitute exceptions to the modified rule, as in them the effect of a cis alkyl group is compared to that of the group in the α -position. Indeed, the velocity values shown by the di- and tri-methylacrylic acids indicate that allocrotonic acid should show a smaller value than methylacrylic acid; that is, cis- β -methyl probably exerts a greater retarding influence than the radical in the α -place. This strong inhibitory effect of cis alkyl group manifests itself in Sudborough and Lloyd's rule for stereoisomers of the type $YHC=CX(COOH)$ (*Ibid.*, 1898, lxxii., 93), in which X and Y are alkyls as the cis-derivatives are esterified very much slower than the trans forms.

Further, Sudborough and Roberts believe that the point on β -chloroallocrotonic acid is "remarkable, as there is very little difference between its constant and that of α -chlorocrotonic acid" (*Ibid.*, 1905, lxxxvii., 1842). In comparing the effect of substituents on the constants of stereoisomeric acids the derivatives of mother substances with similar configurations should be used, otherwise there are two different factors involved in the problem. We should therefore compare α -chlorocrotonic acid (0.163×10^{-5}) with allo- β -crotonic acid (0.438×10^{-5}), where an increase occurs, and the values show that cis β Cl inhibits catalytic esterification to a less extent than do α Cl, which agrees with theory.

The esterification constant (0.905) of allocinnamic acid (1.42×10^{-5}) is only slightly less than that (0.937) of cinnamic acid (3.5×10^{-5}); in α -chlorocinnamic acid (9.7×10^{-5}) and α -chloroallocinnamic acid (107×10^{-5}) the proportionate divergence (0.028 : 0.101) increases, because phenyl in the first acid is in the cis-position to the halogen, and in this neutralizing its negative energy to a larger extent does not increase the negative energy in the carb. xyl to the same degree. It is of interest that the close relationship in the affinity constants of β -chlorocinnamic (28×10^{-5}) and β -chloroallocinnamic (27×10^{-5}) acid is also shown in the esterification constants (0.355 and 0.371) (*Journ. Chem. Soc.*, 1905, lxxxvii., 1843); that is, the relative influences of the phenyl and chlorine in these positions on the acidic hydrogens also extend to the total negative energy in the carboxyls.

Three decades have just passed since the appearance of van't Hoff's "Dix années dans l'histoire d'une théorie" (64), and J. Wislicenus's "Ueber die Räumliche Anordnung u. s. w.," and a backward and forward glimpse at the subject seems in place.

It was unfortunate for the development of stereochemistry that van't Hoff connected it with optical activity through the tetrahedral form of the carbon atom. Lössen (*Ann.*, 1880, cciv., 336, *Ber.*, 1887, xx., 3306) and Auwers ("Entwicklung der Stereochemie," 1899, 22) have shown that the views connected with this shape conception lead to conclusions incompatible with our ideas on dynamic energy, and the writer (*Journ. Prakt. Chem.*, 1886, [2], xliii., 587; 1889 xlii., 209, 384; 1892, lii., 289, 359), that its application by van't Hoff to explain static and dynamic intramolecular atomic relations, and those due to unsaturation, is opposed by innumerable chemical facts. Further, that optical asymmetry is purely a mechanical phenomenon, resulting from the effect of four unequal chemical forces on the atom, and properly belongs to mechano-chemistry (Michael, *Ber.*, 1901, xxxiv., 3647; *Journ. Prakt. Chem.*, 1907, [2], lxxv., 117), (65).

Using van't Hoff's conceptions as the theoretical basis, Wislicenus, in his remarkably lucidly written monograph, developed them in their application to unsaturated compounds in the only possible logical and consistent manner; indeed, it was generally accepted that the configurations of such bodies were definitely and permanently established by the theoretical and experimental investigations of this chemist, and van't Hoff (*loc. cit.*, p. 70) did not hesitate to make this statement without reserve in the above-mentioned book. In the long theoretical and experimental controversy that followed it was finally conclusively proven that all of the configurations of Wislicenus had to be changed (*Journ. Prakt. Chem.*, 1895 [2], lii., 359), as they had been based on the acceptance of cis-processes, whereas in reality trans-processes are the rule. But the new classification showed the inherent weakness of the fundamental stereoisomeric conceptions, as such trans-processes not only find no expression in them but they are in direct conflict with the cis-processes that must be assumed to explain ring formation (*Journ. Prakt. Chem.*, 1895, [2], lii., 289).

As it has been possible to co-ordinate the chemical and physical properties of unsaturated stereoisomers to a very considerable extent with the stereostructures used in these papers, there must be an intimate correlation between them and the spacial relations of the atoms as they actually exist in the molecules. Perhaps the future will solve the difficulties of the present by configurations based on dynamic, instead as now on static conceptions. It is hoped that these papers will draw attention to the chaotic condition of much of the available experimental data that necessarily serve as the basis of theoretical discussion. The physical properties of stereoisomeric compounds, even when they belong to the same carbon series, have seldom been determined under comparable conditions, and their interrelations are often obscured by values obtained from bodies of apparent impurity or by methods of doubtful accuracy. In many cases of great importance the molecular states of aggregation of the substances are unknown, which makes their physical constants of little value for theoretical discussion.

The ideal investigation would start from the simplest derivative from which stereoisomers may be formed by substitution. For instance, with acrylic acid as the mother substance for the monobasic α,β,Δ -acids, and from the properties of products formed by the replacement of α , cis-, and trans β hydrogens, the values of atoms and groups in definite positions to the chemical functions involved in the processes could be ascertained. Although such values would vary somewhat in different compounds, with sufficient experimental data allowance could be made for structural differences, and the relationship between properties and the spacial relations of the atoms could then be traced with far greater certainty than is now possible. Such studies of the physical and chemical properties of stereoisomeric derivatives will give an insight into the mechanism and nature of chemical change, and the

intramolecular atomic relations and mutual influences, to a far greater degree than is possible with any other group of compounds. And as the properties of these isomeric substances depend so obviously on the spacial variations of the atoms, they should help to dispel that curious survival of the type theory that a comprehensive organic theory can be based on the intrarelations of more or less large groups of atoms instead of on those of the atoms themselves (*Journ. Prakt. Chem.*, 1899, [2], ix., 285), whose persistence still not infrequently leads to theoretical conclusions that are incompatible with the facts from which they are drawn.

The law of entropy is valid only in a system that is cooling off, and it is intimately related to the energy transformations connected with changes in the states of aggregation. Hence all *cis*-derivatives in the energy sense strive to pass over into *trans*-compounds, and the transmutations are primarily facilitated by heat, because the assimilated energy assists in overcoming the hindrance to the entropy increase. If a plant were exposed to sufficiently intense extraneous and chemically readily assimilable energy, such as ultra-violet light and certain forms of electric energy, it might bring about a reversion in the energetic relations. The free energy might now be increasing, and the dominant law in such a system would no longer be the entropy principle, but one which may be designated the law of *extropy*.

Under the present conditions the law of entropy represents a resultant, in which the conversion of free into bound energy and heat greatly predominates over the inverse relations. Indeed, it is probable that the extropic energy relations in cosmos have not received the consideration that they merit. Is it not possible, for instance, that a purpose of some of the less refrangible light waves in the economy of nature is to act as diluents to the ultra-violet rays which are so active chemically, and thus prevent the too rapid accumulation of free chemical energy? Or is it not conceivable that in other planetary systems extropy may prevail, and that those mysterious disappearances in space may be connected with too great an accumulation of free energy?

It is because it is possible in the group of stereoisomerides systematically to add or take away energy, that this class of compounds is incomparably better fitted than any other for the study of the relations of energy to properties and chemical structure. In the ability of the chemist in the laboratory to reproduce with them changes in the relations of energy to matter, which are similar to those constantly occurring in nature, is an invaluable means to a better insight into nature's chemical secrets.

Notes.

62. See Friedel (*Bull. Soc. Chim.*, 1877, 2], xxiv., 166, 241), Archibald and McIntosh (*Journ. Chem. Soc.*, 1904, lxxxv., 919), Goldschmidt (*Ber.*, 1906, xxx x., 711), Michael (*Ber.*, 1909, xlii., 311). Base and acid are relative terms, and the oxygen in organic compounds derived from water usually possesses its property of uniting with acids to form more or less stable salt-like addition products. The compound from HCl and $(\text{CH}_3)_2\text{O}$

may be represented by $(\text{CH}_3)_2\text{O} \begin{smallmatrix} \text{H} \\ | \\ \text{Cl} \end{smallmatrix}$, but it is a mistake

to suppose that the bound energy, which in hydrochloric acid holds the elements together (see *Journ. Am. Chem. Soc.*, 1910, xxxii., 991, 1004) is involved in its formation to any extent, or that its existence is not partly due to the interchange between the free energy in the carbons and the hydrogens of the ether and the components of the acid. Indeed, the complicated compositions of many of these addition products are probably due to the formation of "polymolecules" mainly by the neutralisation of free energy of the constituent molecules. The question of when localised addition occurs has been solved in only a

few cases, and there is no doubt that Baeyer's "oxonium theory" is responsible for many formulæ that appeal more to the sense of humour than to that of reason. Kendall and Boorge (*Journ. Am. Chem. Soc.*, 1916, xxxviii., 1735) believe that there is no apparent justification for favouring the localised addition of the mineral acid to the hydroxyl oxygen of the organic acid rather than to the carbonyl oxygen, but it is obvious that the first oxygen is relatively less negative, and if such an addition really takes place it should be at that point. In his interesting papers on such addition compounds Kendall has drawn certain theoretical conclusions, which the facts presented do not seem to warrant. Thus (*Journ. Am. Chem. Soc.*, 1914, xxxvi., 251) the slow sulphonation of aniline, which proceeds only at a high temperature in comparison to the "instantaneous" formation of the double compound of *p*-cresol and sulphuric acid at a low temperature, is in the latter case "in agreement with theory that the reaction is an oxonium salt formation and ionic in its nature." This does not appear to be a correct assumption, for it is not aniline but an acid aniline sulphate that is sulphonated, which is important because it now contains a negative group which protects the nucleus from direct substitution. Numerous organic reactions demonstrate the untenability of the supposed relation between the time element and the "ionic nature" or "oxonium salt formation." For instance, the union of alkyl iodides with alkyl sulphides proceeds from explosive violence at ordinary or instantaneous at a lower temperature, to slow union or inactivity at ordinary temperature, according to the nature of the alkyl radical. Further, the medium may have an enormous influence on the velocity of an organic reaction, and it has been proven that no relation exists between this capacity and its power of ionisation or its unsaturated nature (Menschutkin, Kahlenberg, Michael, and Hibbert, *et al.*). Indeed, in some reactions the velocity is in inverse ratio to the ionisation of the addenda (Michael and Brunel, *Am. Chem. Journ.*, 1909, xli., 118; 1912, xlviii., 267). Generally speaking, it is undoubtedly true that products formed chiefly in the interchange of free energy show a greater velocity formation than those involving proportionately little free and much bound energy. In most cases the energy changes are continuous; that is, the "internal maximum heat" (Wohl, *Ber.*, 1907, xl., 2290) from the conversion of free into bound energy favours instability of the primary product, and more or less rapid rearrangement of the bound energy ensues, with partial transformation into heat energy. Helmholtz's idea that all reactions are "ionic," transferred by Ostwald into organic chemistry without any discrimination or judgment, has been the source of endless futile and unwarranted speculation, and has without doubt seriously hampered the development of organic chemical theory.

63. These views have received further confirmation in the investigation of Baumé and Pamíl (*Comptes Rendus*, 1912, cxv., 426).

64. In memory of J. H. van't Hoff, equally great as a man and a profound and original thinker in Science, the following note from him is published, which was written in English and received with a copy of this book:—"By the same post I take the liberty of offering to your kind attention a little work of mine, that treating on isomerism perhaps may attract notice from your side. If it shortens the distance between your conception of 'alloisomerism' and mine, I shall be amply rewarded. In any case, my compliments and my best wishes for the interesting facts on isomerism that your investigations lay clear."

65. Modifications or further developments of this idea have been advanced by Winther (*Zeit. Phys. Chem.*, 1905, lx., 590, 641, 756), Baly (*Zeit. Electrochem.*, 1911, xvii., 211), Richards (*Journ. Amer. Chem. Soc.*, 1914, xxxvi., 2435), and Wesson (*Ibid.*, p. 2522). There seems no doubt that optical activity would result if four unequal purely mechanical forces could be brought to bear on a carbon atom.

NEW ENGINEERING INDUSTRIES. EXPERTS' SURVEY OF POST-WAR OPENINGS.

THE Engineering Trades (New Industries) Committee of the Ministry of Reconstruction have submitted their report. They were appointed by Dr. Addison in December, 1917, to compile a list of articles (suitable for manufacture by those with engineering trade experience or plant) which were either not made in the United Kingdom before the war, but were imported, or were made in the United Kingdom in insufficient quantities, and for which there is likely to be a considerable demand after the war.

The Committee consisted of sixteen leading engineers and manufacturers, under the chairmanship of the Hon. H. D. McLaren, C.B.E., M.P., but with it was a Labour panel of eleven leading Trade Unionists under Sir Claud Schuster to advise on labour questions likely to arise in the setting up of new industries.

A list of imported articles having been compiled, the Committee found that the best way of proceeding was to set up a number of Branch Committees, each of which could give detailed consideration to a particular group of articles in the list. These Committees were fifteen in number and dealt respectively with (1) Agricultural Machinery; (2) Hollow ware, Sheet Metal, and Pressed Work; (3) Electrical Plant; (4) Machine Tools; (5) Miscellaneous Machinery; (6) Scientific Apparatus; (7) Textile Machinery (sub-divided into eight Branch Committees); (8) Light Section Rolling and Extension; (9) Wire Drawing Machinery; (10) Printing Machinery; (11) Printers' General Machinery; (12) Paper Making Machinery; (13) Leather Making Machinery; (14) Aircraft; (15) Motor Industry. Each Committee consisted of expert members drawn from the industries appropriate to its group, but was presided over by a member of the main Committee. In this way the knowledge and services of some 150 leading manufacturers of the country were drawn upon.

The Committees also worked in close touch with their industries as a whole. From certain industries not represented directly in the fifteen groups special evidence, supplied in reports or by witnesses, was taken. In the case of certain articles of the list it was found desirable to undertake experiments before reporting on the possibility of manufacture. For these, materials and other facilities were obtained through the Ministry of Reconstruction.

The report now issued consists of a report by the Main Committee as a whole and reports from each Branch Committee, dealing with a particular group of manufactures. The Main Committee make certain general observations as to the conditions under which new industries should be set up if they are to develop successfully, touching upon such questions as finance for industry, export trade, foreign competition, the improved methods necessary if British engineers are to maintain a leading position, industrial and scientific research, exhibitions, education, and labour conditions.

The Committee strongly recommend the more extensive adoption of specialisation and standardisation, particularly in the case of small manufacturers who, in their opinion, would do better to confine themselves to the manufacture of a few types of articles which they could then bring to greater perfection and produce more cheaply. The Committee think that such a concentration by each manufacturer on a few types of articles, with proper standardisation, would enable engineering operations to be carried out as "repetition work." This would not only enable many men, highly skilled and highly paid, to be employed in manufacturing the necessary tools and jigs, but would also create an opening for the employment at good wages of a number of unskilled and semi-skilled operatives, both male and female, and wounded soldiers. In this connection the Committee emphasise the importance of co-ordinating manufacture and design, recommending that in future all Government designs and specifications should be considered in co operation with experts in workshop

methods of production. They are of opinion that in the absence of special circumstances Government departments and public authorities should order standard goods of British manufacture, and that in cases where there is no question of ordering standard design they should have in view the encouragement of the production of articles of new and improved types or of experimental design.

In order to stimulate production the Committee consider that both employers and workpeople should be educated both generally and specially: Employers and staff, in regard to what is being done in up-to-date works where quantity production under scientific management is carried on, and workpeople, to remove the impression that quantity production produces unemployment, and to make them realise the national importance of producing the maximum output in the minimum time.

The Committee concur in a number of conclusions drawn by the Labour Advisory Panel, and recommend that new industry should not be introduced into this country unless the wages paid to those employed in it are such as to insure an adequate standard of living and unless machinery exists or can be set up for regulating rates of wages and hours of labour; further, that no industry be introduced under conditions involving any special liability on the part of those engaged in it to industrial disease.

Incidentally light is thrown upon the restrictive effects of legislation in the past upon the development of British industries, and upon other conditions such as the incidence of taxation, dumping, &c., which, in the opinion of those engaged in engineering, stand in need of reform.

The report then gives summaries of the reports presented by the various Branch Committees. In view of the newly recognised importance of agriculture in this country the report of the Branch Committee on Agricultural Machinery will be of interest. While they consider that this industry was on the whole in a fairly satisfactory condition before the war, they think that there is room for considerable development, both in home and export trade. They draw special notice to the motor tractor industry, which is more highly developed in the United States than in this country. Several British firms were devoting attention to this production before the war, but Government demands upon them for munitions greatly retarded the development of the industry. The result of the importations by the Government and private firms of American tractors on an immense scale is watched with some anxiety. Many firms are preparing to manufacture them and they will be produced here in large quantities as soon as the necessary raw materials and labour are available. In view, however, of the advantageous start given to the imported article, due largely to Government action, it is very important that every facility and encouragement should be given to British makers at the earliest possible moment. Amongst other agricultural articles the manufacture of which could in the Committee's opinion be greatly developed are cream separators, swath turners, hay loaders, disc harrows, and corn and seed drills.

The Branch Committee on Hollow-ware, Sheet Metal, and Pressed Work, in a detailed report on 65 branches of manufacture, consider that only a small percentage of highly skilled labour is required in this branch of industry, mainly for tool making and repairing. Of the remaining labour, having regard to the amount of physical strength and mechanical aptitude required, women to the extent of about 50 per cent could be employed. Among the many articles dealt with by this Committee are sewing machines and typewriters. Large firms are known to be taking up the manufacture of the former, and it is believed that they will be adequately manufactured in this country, but there is room for considerable development in the manufacture of typewriters.

Interest also attaches to the report of the Branch Committee on Electrical Apparatus and Machinery, who consider that as regards most of the articles under their consideration ample manufacturing facilities exist, and in many cases did exist before the war, for meeting the whole

requirements of the United Kingdom and Colonies and, in certain cases, for meeting the export trade to other countries, but that these facilities were not fully employed owing to the importation of articles from abroad. They lay special stress upon the necessity for ensuring the continuance of the manufacture of carbons and attach a special report as an appendix which points out that had it not been for the action of one firm on continuing to make arc lamps carbons at very considerable loss to themselves, the country would have had considerable difficulty in meeting the demands for searchlight carbons. With regard to magnetos, now adequately made in this country, the Committee recommend that German magnetos should be excluded for a period after the war, except under licence, and that a duty should be imposed on all imported magnetos.

The Branch Committee on Scientific Apparatus point out that the scientific apparatus industries are vital to the nation during peace and war. No country can remain for long in the front rank industrially if it depends upon others for its scientific apparatus, because such apparatus is generally produced where science is most actively applied in industry. The Committee gives a long list of articles which are not adequately manufactured in this country, and in regard to which there is room for new industries. One such industry is the manufacture of clocks and watches on a large scale. They consider the establishment of such an industry of very considerable importance. In Switzerland, Germany, and the United States, these manufactures, turned out in large quantities and cheaply, constitute the chief training ground for skilled mechanics accustomed to work of the highest precision and finish. In this country, which has no such training ground, the scientific apparatus industry suffers from lack of such skilled help and manufacturing experience.

The Branch Committee on Aircraft Machinery consider that owing to the enormous expansion of the industry during the war, its output capacity will be greater than the demand for years to come, and advise that immediate steps should be taken by the Government to avoid the extinction of so essential an industry. Proposals to this end have been forwarded to the Government.

Valuable technical information is contained in the reports presented by the Branch Committees on Textile Machinery. Generally speaking, textile machinery was adequately manufactured in this country, but the articles taken up by the Branch Committees were textile machines of a highly specialised kind, in the making of which there seemed room for further development. Amongst the machinery dealt with is that required for calico printing, dyeing, hank mercerising, flannelette raising, gas mantle yarns, silk waste, lace and embroidery making, latch needle making, &c.

The Branch Committee on Machine Tools and Small Tools give a list comprising a number of machines which are not adequately made in this country, and in the making of which there is room for further development. Among these are mechanics' fine tools, portable electric tools, lathe and drill chucks, and many other kinds of machine tools.

It is impossible to summarise all the Branch Committees' reports in a newspaper article. Generally speaking, however, they go to show that whilst in many fields British industry was more firmly established and more successful than is sometimes supposed, there are, nevertheless, in nearly all directions openings for manufacturers with enterprise.

The Committee have agreed that bona fide enquirers interested in the manufacture in Britain of any particular article may be put in touch with the Chairman of the Branch Committee concerned to obtain such information as is available and advice as to their prospects in entering upon a new field of industry. Such enquirers will be able to obtain at the Ministry of Reconstruction all the information made available by the Branch Committees, except that which is of a confidential nature.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, January 30, 1919.

Sir J. J. THOMSON, President, in the Chair.

The following papers were read:—

"An Investigation of Extreme Ultra violet Spectra with a Vacuum Grating Spectrograph." By Prof. J. C. McLENNAN, F.R.S., and R. J. LANG.

In this investigation the vacuum-grating spectrograph used was designed and constructed by the Adam Hilger Co. The grating had a ruling 2.5 cms. wide and 1.9 cm. in length, of 20,000 lines to the inch. Its radius of curvature was 120 cm.

The vacuum arc spectra of mercury, copper, iron, and carbon were investigated. With carbon, wave-lengths were observed and measured down to $\lambda = 584$ A.U.

"On the Absorption Spectra and the Ionisation Potentials of Calcium, Strontium, and Barium." By Prof. J. O. McLENNAN, F.R.S., and J. F. T. YOUNG.

In this paper it has been shown that the wave-lengths constituting the series $\delta = (1.5, S) - (m, P)$, which are strongly absorbed by the vapours of calcium and strontium, are also strongly absorbed by the vapour of barium.

The wave lengths of this series are as follows:—

m	2	3	4	5	6
$\lambda(\text{A.U.}) =$	5535	3275	2845	2597	2542
$\delta =$	10864.5	30534.4	35119.4	35502.1	39339.1

m	7	8	9	10
$\lambda(\text{A.U.}) =$	2198	2170	2155	2141
$\delta =$	40032	40486	40733.2	40966.8

The wave-length of frequency $\delta = (1.5, S)$ for barium has been shown to be $\lambda = 2380.56$ A.U., and the wave-lengths of the two series $\delta = (2.5, S) - (m, P)$ and $\delta = (3.5, S) - (m, P)$ have been calculated.

The wave-length of frequency $\delta = (1.5, S) - (2, P_2)$ has been deduced as $\lambda = 7901.11$ A.U.

Assuming that the ionisation potential for barium is given by the relation $V_0 = h\nu_0$, where $\delta = (1.5, S)$, the value of this magnitude for barium has been calculated to be 5.21 volts.

"Vacuum Arc Spectra of Various Elements in the Extreme Ultra-violet." By Prof. J. C. McLENNAN, F.R.S., D. S. AINSLIE, and D. S. FULLER.

The experiments described were carried out with a fluorite spectrograph whose optical train consisted of a 60° prism and two biconvex lenses of 15 cm. focal length.

The vacuum arc spectra of copper, zinc, aluminium, carbon, thallium, tin, lead, iron, cobalt, nickel, and cadmium were investigated between $\lambda = 2400$ A.U. and $\lambda = 1400$ A.U. The measurements obtained for the vacuum arc spectra of copper, zinc, cadmium, and aluminium are well covered by the results for the spark spectrum of these metals, as obtained by previous workers.

For tin, lead, and thallium the results agree fairly well with those given by Saunders from $\lambda = 2400$ A.U. to $\lambda = 1700$ A.U. Below the region covered by Saunders' work many new lines were observed and measured.

The measurements for the vacuum arc spectra of iron, cobalt, nickel, and carbon appear to be the first obtained for the arc spectra of these substances in the Schumann region. For these spectra nearly all the measurements between $\lambda = 2400$ A.U. and $\lambda = 1850$ A.U. as given in the paper are covered by previous work on their spark spectra. Within the region between $\lambda = 1850$ A.U. and $\lambda = 1400$ A.U. a number of new lines were photographed and measured.

"Emission and Absorption in the Infra red Spectra of Mercury, Zinc, and Cadmium." By R. C. DEARLE.

In the investigation described in this communication

the absorption spectra of mercury, zinc, and cadmium were studied with a Hilger Infra-red Spectrograph provided with a rock salt prism and a linear thermopile, in conjunction with a Paschen Galvanometer made by the Cambridge Scientific Instrument Co. With each of the vapours the range investigated lay between $1.0\ \mu$ and $1.6\ \mu$.

In studying the emission spectrum of mercury vapour bombarded by electrons, it was found that radiation of the wave-length $\lambda = 10140\ \text{\AA}$ was emitted with impact voltages as low as 5 volts, and evidence was also obtained indicating that mercury vapour could be made to emit radiation of this wave-length with impact voltages less than 5 volts. The paper presents some considerations in support of the view that while mercury has an ionisation potential of one type of $10.4\ \text{volts}$, it may also have an ionisation potential of a second type of about $2.5\ \text{volts}$.

"The Measurement of Magnetic Susceptibilities of Low Order." By ERNEST WILSON.

1. An Instrument which has been designed for the measurement of magnetic susceptibility of low order. It depends for its action upon the pull exerted by an electromagnet in accordance with the well-known Maxwell expression for the mechanical force exerted upon unit volume of the substance. This mechanical force is balanced against the force of torsion in a phosphor-bronze strip.

2. The instrumental constant is determined from data obtained directly with the instrument itself, and by the employment of substances whose susceptibilities had been measured by other methods. A modified method of using a ballistic galvanometer has been devised which leads to greater sensitiveness. Rock specimens and other substances have been used, and some interesting results obtained. It is shown that the susceptibility of 13 per cent manganese alloy is much smaller than usually supposed.

3. The susceptibility of powdered rock specimens has been measured and compared with the solid. A very fair agreement has been obtained between the two, and the method has the advantage that powders can be rapidly made.

4. The susceptibilities of varieties of mica have been measured, and it is shown that in certain cases, in a direction parallel with the laminae, the susceptibility may be over 50-fold that obtained in a direction at right angles thereto.

5. A series of light aluminium alloys has been tested, and it has been found that whereas the susceptibility of commercial aluminium is increased by alloying with copper and manganese, it is diminished by alloying with cobalt.

6. It is shown that the balance could be used to rapidly determine the relative amounts of ferrous iron in different specimens of glass.

7. Certain specimens of tourmaline have been examined. The green and dark blue opaque varieties have susceptibilities in the direction of the principal crystallographic axis varying from 16 to 20 per cent less than in a direction at right angles thereto. The susceptibility of rose-coloured tourmaline is very small in comparison.

8. The paper concludes with a note on the retentivity of rock specimens and its possible influence upon magnetic disturbances in magnetic survey work.

"An Experimental Determination of the Ionisation Potential for Electrons in Helium." By F. HORTON, D.Sc., and ANN C. DAVIES.

An investigation of the minimum potential difference through which an electron must fall in order to be able to ionise an atom of helium on collision with it, has been made by methods capable of distinguishing between ionisation of the gas and secondary effects due to radiation.

It has been found that radiation is produced when electrons having a velocity of $20\frac{1}{2}\ \text{volts}$ collide with

helium atoms, and that this is not accompanied by any ionisation of the gas.

It has also been found that ionisation of the helium does not occur until the velocity of the electrons is raised to $25.6\ \text{volts}$, and that no other type of radiation is produced at this point.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Annual General Meeting, February 5, 1919.

Dr. SAMUEL RIDEAL, President, in the Chair.

THE PRESIDENT delivered his annual Address.

The following were elected as Officers and Council for the ensuing year:—

President—Samuel Rideal.

Past-Presidents—Serving on the Council (Limited by the Society's Articles of Association to eight in number)—Leonard Archbutt, Edward J. Bevan, A. Cnaston Chapman, Bernard Dyer, George Embrey, Otto Helmer, E. W. Voelcker, J. Augustus Voelcker.

Vice-Presidents—W. T. Burgess, G. N. Huntly, Alfred Smetham.

Hon. Treasurer—Edward Hinks.

Acting Hon. Treasurer—E. W. Voelcker.

Hon. Secretaries—P. A. Ellis Richards, E. Richards Bolton.

Other Members of Council—W. Bacon, W. J. A. Butterfield, H. G. Colman, G. D. Elsdon, R. Hellon, D. Lloyd Howard, H. Hurst, C. A. Keane, W. H. Simmons, W. Lincoln Sutton, G. Rudd Thompson, J. F. Tocher.

Ordinary Meeting, February 5, 1919.

Dr. SAMUEL RIDEAL, President, in the Chair.

Certificates were read for the first time in favour of Messrs. Robert Odell Bishop, A.I.C., Hubert William Bywaters, D.Sc., F.I.C., Ph.D., Robert Atkinson Oddy, Charles Kenneth Tinkler, D.Sc., F.I.C.

A certificate was read for the second time in favour of Mr. Cecil William Wood.

The following were elected Members of the Society:—Messrs. S. H. Blichfeldt, John Clare Eastick, A.I.C., Robert Howson Pickard, D.Sc., Ph.D., F.I.C., Lionel Guy Radcliffe, M.Sc., F.I.C., James Smith, Frank Edwin Weston, B.Sc.

The following papers were read:—

"Technique of Iodine Determinations; with a Note on a New Machine for Sub-dividing Oleaginous Seeds." By JOHN ALLAN.

In certain processes involving changes in the composition of oils, control is obtained by determination of the iodine value. The sequence of operations is described, and the arrangements made to secure the carrying out of a large number of iodine value determinations in a minimum of time.

The sub-division of certain varieties of oleaginous seeds preparatory to analysis is attended with difficulty, as they easily form pastes which clog ordinary milling machines, and give a product the extraction of which is highly unsatisfactory. The machine described overcomes this and other difficulties, and besides being easy to operate, gives a product in a highly suitable condition for subsequent treatment in analysis.

"Recovery of Nessler Reagent." By D. PULLMAN.

The whole of the mercury and iodine is recovered from use of Nessler solution by the addition of a soluble mercury salt to the neutralised residues.

The mercuric iodide thus obtained is converted by means of metallic zinc into zinc mercuric iodide and mercury.

The double salt, with the addition of sodium hydroxide, forms an efficient nesslerising reagent, whilst the mercury is dissolved in nitric acid and used to precipitate further residues.

NOTICES OF BOOKS.

The Industrial League Journal. Vol. 1., Nos. 1 and II. London: Published by the League at 56, Victoria Street, S.W.

THE aims of the Industrial League are so unquestionably laudable that it is much to be hoped that it will receive the cordial sympathy and support of the public, and that the promoters on their side will choose judiciously the means of attaining them. The League exists for the purpose of bringing about a better understanding between employer and employed, and the journal will do useful service in spreading knowledge and helping to educate in the truest sense of the word. The first and second numbers reach a high standard of excellence, and well-known men have contributed valuable articles to them, the Foreword to the first number having been written by the Rt. Hon. G. H. Roberts, M.P. The same number contains a full report of the proceedings at the first of a series of Conferences arranged by the Industrial League and held recently in London.

New Reduction Methods in Volumetric Analysis. By EDMUND KNECHT, Ph.D., M.Sc.Tech., F.I.C., and EVA HIBBERT, M.Sc.Tech. Reissue with Additions. London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. 1918. Pp x+135. Price 5s. net.

THIS monograph contains detailed accounts of all the work the authors have done on the use of titanous chloride as a quantitative reducing agent for various determinations. Its applications include estimations of metals, non-metallic elements, and organic compounds, such as dyes, sugars, &c., and full details are given which will enable students using the book to obtain accurate results after a little practice. In the new addition about thirty pages of matter have been added in the form of an addendum, and the new determinations include the estimation of sulphurous acid in sulphites and bisulphites, the estimation of nitrates and nitro-compounds, and some other useful applications of titanous chloride which have recently been worked out by the authors. Of these, the estimation of alizarin on dyed cotton fabrics is particularly interesting, and will very probably be extensively employed.

CORRESPONDENCE.

SOLDERING FLUXES.

To the Editor of the Chemical News.

SIR,—I beg to inform you that I am in receipt of a communication from the United States which reads as follows:—

We are manufacturers of Nokorode soldering flux, in which we do a very large business, both domestic and export. We desire to get the fullest possible information to enable us to judge the possibility of establishing a profitable trade with your city and vicinity. The main points on which we wish you would furnish us all possible details are as follows:—

Is the market a large and favourable one for soldering fluxes?

What is the approximate volume of business done there in this line?

What class of flux is in most common use, liquid, dry or paste, acid, resin or resinous?

What special brands are there on that market, and which, if any, has the preference?

In what form are they marketed and in what style and size containers?

Where are they made and by what firms, and what are the wholesale and retail prices?

Are there any large manufacturing concerns in your city or neighbourhood whose business is such as to call for large quantities of flux; in other words, who do a great deal of soldering, what kind do they use, and of whom do they buy, and what particular line or lines of business are they in?

We want all possible information, general and specific.

If you can furnish me with any information along the above lines, or, in the contrary event, advise a likely source from which the same may be obtained, I shall greatly appreciate the courtesy.—I am, &c.,

ROBERT P. SKINNER, American Consul General.

18, Cavendish Square, London, W. 1,
February 7, 1919.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cixvii., No. 20, November 11, 1918.

Method of Estimating Metals by Electrolytic Deposit without the Use of External Electric Energy.

Maurice François.—If a solution of a metallic salt to which sulphuric acid has been added is placed in a platinum crucible, and a rod of zinc or aluminium is suspended in the solution so as not to touch the bottom of the crucible, a current is set up, and a deposit of the metal contained in the salt is obtained and can be weighed. To determine silver or gold the solution must contain potash and potassium cyanide and ammonia as well as the salt to be determined, while with mercury the liquid must consist of sulphuric acid containing a small proportion of potassium iodide. The operation takes twenty-four hours and the results obtained are exact.

No. 21, November 18, 1918.

Determination of Lactose.—E. Hildt.—In the hydrolysis of lactose phenol or benzene sulphonic acids, used in the form of barium or sodium salts, in presence of a corresponding quantity of sulphuric acid, give excellent results. The hydrolysis is complete after heating for three and a-half to four hours.

No. 22, November 25, 1918.

Solubility of Cupric Hydrate in Sodium and Potassium Hydroxides.—Justin Mueller.—Cupric hydrate has been supposed to be insoluble in NaOH or KOH, except in presence of organic substances such as tartaric acid, but as a matter of fact the presence of organic substances is not indispensable. In well defined quantities cupric hydrate is completely soluble in sufficiently concentrated solutions of KOH and NaOH, the solutions obtained are quite stable and are not affected by heat, even after they have been diluted. The concentration for NaOH is 37–39° B., or a density of 1.345–1.370; for KOH 45–48° B., or a density 1.453–1.498. If the concentration is diminished or the proportion of copper increased solution is not complete.

New Synthesis of Aromatic from Fatty Compounds.—Tel. Komrinos.—When malonyl chloride reacts with acetone in presence of marble two substances are obtained—phloroglucine and a compound of formula

$\text{Cl.CO.CH}_2\text{CO.CH}_2\text{CO.CH}_3$, which is readily transformed into phloroglucine, losing a molecule of hydrochloric acid under the action of marble. The constitution of phloroglucine is thus verified and an easy method of passing from fatty to aromatic compounds is provided. It seems probable that the synthesis can be generalised.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 3rd inst., Sir James Crichton-Browne, M.D., LL.D., F.R.S., Treasurer and Vice-President, in the Chair. The Chairman reported a bequest of £300 from the late Dr. T. Lambert Mears, who was a Member of the Institution for fifty-three years, and a donation of £50 from "An Old Member" in celebration of his fiftieth year of membership. Mr. A. J. Walter, K.C., was elected a Manager to fill the vacancy caused by the death of Sir Charles Norris Nicholson, Bt., M.P.

Royal Institution.—Next Tuesday, February 18, at 3 o'clock, Captain G. P. Thomson will give the first of two lectures at the Royal Institution on "Aeroplanes in the Great War." On Thursday, February 20, Prof. H. M. Lefroy will give the first of two lectures on "Insect Enemies of our Food Supplies"; the second, on Thursday, February 27, on "How Silk is Grown and Made." The Friday evening discourse on February 21, at 5.30 o'clock, will be delivered by Mr. A. T. Hare on "Clock Escapements"; on February 28, by Prof. J. A. McClelland on "Nuclei and Ions." On Saturday, February 22, at 3 o'clock, the Hon. J. W. Fortescue will give the first of two lectures on "The Empire's Share in England's Wars."

MEETINGS FOR THE WEEK.

MONDAY, 17th.—Royal Society of Arts, 4.30. "Scientific Problems of Electric Wave Telegraphy," by Dr. J. A. Fleming.

TUESDAY, 18th.—Royal Institution, 3. "The Development of Aeroplanes in the Great War," by Capt. G. P. Thomson, M.A.

— Institution of Petroleum Technologists, 5.30. "The Financing of Oilfields," by M. Summers.

WEDNESDAY, 19th.—Royal Society of Arts, 4.30. "Use of Electricity in Agriculture in Germany," by J. F. Crowley.

THURSDAY, 20th.—Royal Institution, 3. "Insect Enemies of Our Food Supplies," by Prof. H. Maxwell Lefroy.

— Royal Society, 4.30. "The Metabolism of the Glucosides of the Arbutin Group," by J. Dufrenoy. "Dental Changes in the Teeth of the Guinea pig produced by a Scorbatic Diet," by S. S. Zilva and E. M. Wells. "New Factor in the Mechanism of Bacterial Infection," by W. E. Bullock and W. Cramer. "Distribution of the Serological Types of *B. tetani* in Wounds of Men who received Prophylactic Inoculation, and a Study of the Mechanism of Infection in, and Immunity from Tetanus," by Major W. J. Tulloch. Chemical Society, 8.

FRIDAY, 21st.—Royal Institution, 5.30. "Clock Escapements," by A. T. Hare, M.A.

SATURDAY, 22nd.—Royal Institution, 3. "The Empire's Share in England's Wars—Western Empire," by The Hon. J. W. Fortescue.

Experienced Research Chemist and Analyst. with excellent Laboratory facilities in City, is now free to undertake RESEARCHES connected with the manufacture of CHEMICALS, INTERMEDIATES, DYES, &c.; also the Utilisation of WASTE PRODUCTS and all classes of ANALYSIS.—"Laboratory," 7, 8, & 9, Rolt Court, Fleet Street, London.

Wanted, one Siemens and Halsk HYDROMETER, New or Secondhand. State full particulars, condition, price.—Address, "Hydrometer," Wm. Porteous and Co., Advertising Agents, Glasgow.

FRANCE (BORDEAUX and SUD-OURST).—Representations wanted by French Engineer Chemist of good firms (for Chemical Products, Chemical Machineries, Chemical Apparatus, New Processes).—Address TESSIER, 201, Cours Balguerie, Bordeaux.

A Discharged Soldier seeks situation as Works Chemist, or Laboratory Work, practical and theoretical experience. Good testimonials.—Address, D. S., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Analytical and Consulting Chemist, M.Sc., A.I.C. (Food and Drugs), will buy existing Practice or purchase Partnership with view to extension.—Address, Box 135, W. H. Smith and Son, Kingsway, London, W.C. 2.

Analytical Chemist with considerable experience, just released from Government work, wishes for a Position with an established firm, and would also consider Partnership with same or with Chemist who has had previous experience in Private Practice Work with view to opening out.—Address, "Analytical," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Assistant Works Manager seeks progressive Position with Chemical Firm. Fully qualified Chemist. Twelve years' very varied Works experience. Good knowledge of Engineering. Accustomed to administration. Address, A. W., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Chemist (25), ex-Army N.C.O. (1915-16), desires Appointment at home or abroad in Works or Laboratory. Can control labour; good Analyst. Two and a-half years in large Government Factory.—Address, B., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Chemist for Works Laboratory, with experience in the Electrolytic Analysis of Copper Alloys. The vacancy offers excellent opportunities for an ambitious man with an aptitude for Engineering. Applicants should be between twenty and twenty-five years of age. State age and experience.—Address, "Electrolytic," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

CHEMIST.—Well qualified to conduct Organic Research Work in a London Factory Laboratory. State age, experience, and salary required.—Address, "Investigator," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Ex-Officer, disabled, four years experience of Analysis, including Foods and Drugs, requires responsible Position.—Address, N. O., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Inter. B.Sc. requires post in Chemical Works or Laboratory, in or near London. Lately demobilised as student. Address, W. G. B., 7, Livingstone Road, Clapham Junction, S.W. 11.

London Honours Graduate, A.I.C., twenty years' experience Foodstuffs, General Analysis, and Bacteriology, now supervising Works Laboratory, desires responsible progressive Post where energy and initiative will meet with recognition.—Address, L. H., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Required for Works Laboratory (ten miles North of London).—

One Works Chemist, to have charge of all Routine Testing;
One Junior, aged 17-19, must have matriculated with Chemistry as subject.

One Senior Analyst, for General Analytical Work;
One Junior Analyst, for General Analytical Work;
One Process Chemist, for general Process Investigations.

The work will be almost entirely Inorganic in character. Applicants must be accurate workers and have had sound experience. University-trained men preferred. Give full particulars and state salary required.—Address, N.L. 10, CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Trained Research Chemist, with Works experience, seeks Employment with Manufacturing Firm; or would make good Assistant to Private Investigator. London Degree, two languages; microscopy.—Address, T. R., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Works Chemist wanted by Fine Colour, Paint, and Chemical Manufacturers in country district near London. Applicants must be under thirty, capable of training and controlling small number of employees and becoming the right-hand of energetic Managing Director. Business as well as Scientific ability essential. Salary £250 and commission. State qualifications, experience, &c.—Address, "Paint," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Works Analytical Chemist required. One conversant with Soap Manufacture, Nicotine Extractions, and Agricultural and Horticultural Preparations. State full particulars and salary required.—Address, W. A., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

THE CHEMICAL NEWS

VOL. CXVIII., No. 3971.

THE CONCEPTION OF THE CHEMICAL ELEMENT AS ENLARGED BY THE STUDY OF RADIO-ACTIVE CHANGE.*

By FREDERICK SODDY.

THE Council of the Chemical Society have honoured me with the invitation to deliver one of three lectures bearing on the ultimate constitution of matter, and I accepted the invitation in my desire to show how greatly I appreciated it rather than with any prospect of being enabled, when the time came, to say anything on the subject which has not already been said before. The problem of the ultimate constitution of matter belongs to another world than that through which for the past four years we have been living, and although hostilities have at length ceased, and we may look forward to an opportunity of resuming in the future the thread of our philosophical investigations, philosophy herself is not so easily to be resumed. Novel in one sense as are the ideas introduced into the concepts of physics and chemistry by the study of radio-activity, four years' interruption has made them appear rather as a remote historical accomplishment than as a contemporaneous development. Although no longer new, however, the more as the subject matures does it become apparent that these advances are of fundamental and increasing importance to the chemist.

One would perhaps have expected that on the first and most fundamental conclusion arrived at in the study of radio-active change that the change is of a transmutational character, involving the spontaneous disintegration of the radio-element into others, it would have been the chemists who would have been most deeply interested, and who would have weighed the evidence and pronounced a decision. Yet judgment on the view, which was put forward more than fifteen years ago, on evidence in my opinion even then deserving of serious consideration, although accepted and universally adopted by the workers in the subject and by physicists, has gone by default so far as the majority of chemists are concerned. From the first, much of the most important evidence has been of singularly simple and convincing chemical character.

The Transmutational Character of Radio-active Change.

If a chemist were to purify an element, say lead from silver, and found, on re-examining the lead at a later date, that silver was still present, and, again and again, repeating the process, found always that silver, initially absent, reappeared, would he not be forced to conclude that lead was changing into silver and that silver was being produced by lead? It is because of the absence of evidence of this kind that the doctrine of the unchangeability of the elements has grown up. One positive example of the kind in question and that doctrine would be at an end. The conclusion to which in 1902 Sir Ernest Rutherford and I were forced with regard to the element thorium was based on evidence of this direct and simple nature. By simple purification, by chemical and physical means, constituents responsible for the greater part of the radio-activity of thorium can be separated, and as often as they are separated they are regenerated at a perfectly definite and regular rate. One of these constituents, the emanation, is gaseous, and it can be separated from the thorium by more elaborate means than by a puff of air. Certainly the actual quantity of thorium emanation is infinitesimal,

but this did not hinder its complete chemical characterisation, for it was found to pass unabsorbed through every reagent tried, one or other of which would have absorbed every known gas with the exception of the gases of the argon family. The conclusion that the thorium emanation was a gas of the argon family produced by thorium, later extended to the similar gaseous products of radium and actinium, was a purely experimental conclusion reached before any theory whatever as to the nature of radio-activity had been advanced.

Another constituent responsible for part of the radio-activity we called thorium-X. It is left in the filtrate when a solution of thorium is precipitated with ammonia, although not when the thorium is precipitated by other reagents, such as sodium carbonate or phosphate. After this removal, however, thorium-X re-forms in the thorium. Moreover, it is thorium-X, not thorium, that produces the emanation. The latter in turn produces the non-volatile active deposit, in which the successive products, called thorium-A, -B, -C, and -D, are now recognised. The false interpretation of a similar phenomenon in the case of radium, before the radium emanation had been recognised, led to the view that inactive matter could be rendered temporarily radio-active by "induction," through contact with or association with radio-active matter. In the case of thorium, the discovery of the chemical character of the thorium emanation rendered the nature of the phenomenon clear almost from the first.

This, taken in conjunction with the atomic character of radio-activity, recognised by Mme. Curie from the start, and with the fact that the law of radio active change proved to be the same as the law of unimolecular reaction, made the conclusion that the radio-elements were undergoing a series of successive changes, in which new elements are produced, of chemical and physical character totally distinct from those of the parent element, the only one capable of explaining the facts.

Novel and unexpected as it was to find transmutation spontaneously in progress among the radio-elements, the phenomena this explanation explained were equally novel and transcended what to a generation ago would have appeared to be the limits of the physically possible.

It is to pay chemistry a poor compliment to represent this conclusion as in any way contrary to the established foundations of chemistry. If it had not been for the correct conception of the nature of chemical change, the clear distinction between atoms and molecules, and the conclusion that in all changes in matter hitherto studied the element and the atom of the element remain essentially unchanged, which we owe to the founders of chemistry, the character of radio-activity would not have been arrived at so quickly. On the other hand, if radio-activity had not been almost instantly recognised as a case of spontaneous transmutation, then, if you will, there would have been something radically wrong with chemistry and the training it affords in the elucidation of the metamorphoses of matter.

With regard, however, to the various claims that have been made since that transmutational changes can be artificially effected, by the aid of the electric discharge in gases or the rays from radium, I have always regarded the evidence in this field as capable of simple alternative explanation. Different investigators have obtained entirely opposite results, and there is not that consensus of evidence one finds among those who have investigated radio-active change.

In another direction there has been a tendency to understate the unique and unparalleled phenomenon of radio-active change, and to connect what is entirely and solely a development of the new experimental science of radio-activity, with the somewhat older isolation of the electron and the electronic hypotheses of the constitution of matter to which that discovery have given rise. For example, Sir J. J. Thomson in his Romanes Lecture, 1914, says: "Since the electron can be got from all the chemical elements we may conclude that electrons are a constituent

* A Lecture delivered before the Chemical Society, December 19, 1918.

of all the atoms. We have thus made the first step towards a knowledge of the structure of the atom and towards the goal towards which since the time of Prout many chemists have been striving, the proof that the atoms of the chemical elements are all built up of simpler atoms—primordial atoms, as they have been called." The removal of electrons from matter occurs in physical, chemical, and radio-active changes alike, exemplified, respectively, by the electrification of a glass rod by friction, the ionisation of an electrolyte by solution, and by the β -ray change of radio-active substances. It is only in the latter case, however, that the electron can be regarded as a primordial constituent and the change as transmutational. Even to-day it is in radio-active phenomena, and in these alone, that the limits reached long ago in the chemical analysis of matter have been overstepped, and the Rubicon, which a century ago Prout vaulted over so lightly in imagination, has actually been crossed by science.

First and Second Phases of Development.

Looking backward to the first recognition of the character of radio-active change in 1902, it is possible to distinguish broadly two phases. The first phase, concerned mainly with the disentangling of the long and complicated series of successive changes, commencing with the two primary radio-elements uranium and thorium, and including ultimately all the known radio-elements, added little to the conceptions of chemistry beyond the disturbing fact that the radio-elements, although in every other respect analogous to the ordinary elements, are in process of continuous transmutation. But in the second and more recent phase of radio-active change, the study of the chemical character of the successive products and the law connecting this with the type of ray expelled in the change, the discovery of elements with different radio-active but identical chemical character, the recognition of these as isotopes or elements occupying the same place in the periodic table, and the interpretation of the significance of the periodic law, conceptions are arrived at which are not merely novel, but upsetting. In this phase, an aspect of the ultimate constitution of matter has been revealed that, although well within the scope of the conceptions of elements and atoms which we owe to the nineteenth century, nevertheless has totally escaped recognition. I am not much concerned with definitions, but I think the Chemical Society might safely offer a prize of a million pounds to any one of its members who will shortly and satisfactorily define the element and the atom for the benefit of and within the understanding of a first year student of chemistry at the present time.

Chief Features of Radio-active Change.

The features that distinguish radio-active change from chemical change, and which have made it possible in a few short years to reduce to some degree of finality and completeness the intensely complicated series of successive changes suffered by the elements uranium and thorium in the course of their disintegration, are chiefly two. In the first place, the whole phenomena are inevitable, incapable of being changed or deviated from their allotted course by any means whatever, independent of temperature, concentration, or the accumulation of products of reaction, the presence of catalysts, irreversible, and capable of being accurately and quantitatively followed without alteration or disturbance of the changing system. The mathematical theory, although for many successive changes it becomes cumbersome and unwieldily to a degree, involves only the solution of one differential equation by a device quite within the compass of anyone possessing a knowledge of the bare elements of the calculus to employ. The second feature is the magnitude of the energy evolved, which, weight for weight of matter changing, surpasses that evolved in the most exothermic chemical changes known, from one hundred thousand to a million times. Manifested in the form of rays, by their fluorescent, photo-

graphic, or ionising power capable of being put into evidence in almost inconceivably minute amount, changes are capable of being followed, and by the electroscopes accurately measured, which would conceivably require to continue for millions of years before they could be experimentally detected by chemical or even by spectroscopic methods. The disintegration of the single atom is ascertainable, for example, in the spintharoscope of Sir William Crookes, where each of the scintillations separately visible is due to the impact of a single α -particle on the zinc sulphide screen. On the same principle, methods have been developed and are in regular use for counting the number of atoms disintegrating per minute, whereas to the spectroscope at least 3×10^{13} atoms as a minimum must be present, 25,000 times as many atoms as there are human beings alive in the world, before any element can be so detected. By the most curious compensation, almost of the nature of a providential dispensation which some may have found difficult to believe, the quantity of matter of itself is not of importance in investigating radio active change. The methods depend on the rate of emission of energy, and this is proportional to the quantity of the changing element multiplied by its rate of change. In the disintegration series, the various members accumulate in quantities inversely proportional to the rates of change, and so it comes about that all changes within the series are equally within the scope of the method whether, as in the case of the parent elements, they involve periods surpassing the most liberal estimates of the duration of geological time or, as in the case of the C' members, are estimated to run their course in a time so short that light itself can travel but a very few millimetres, before the next change overtakes the changing atom.

The condition of radio-active equilibrium in which the quantities of the successive products assume the above stationary ratio is of course entirely different from chemical equilibrium, and is the condition in which for each member of the series except the first as much is produced as changes further in the unit of time.

The foregoing applies so long as the changes continue. When they are finished and it is a question of ascertaining the ultimate products, the task may be likened to that of searching for a meteor which a moment before lit up the heavens and now has vanished into the night.

The Ultimate Products.

It is a matter for surprise that in all radio-active changes so far studied there appear to be only two ultimate products, helium and lead, the former constituting the α -particles and the latter being produced both by uranium and thorium, withal, as we now know, not the same lead in the two cases. There are sufficient experimental reasons for doubting whether the disintegration of an atom into more nearly equal parts would be within range of detection by any of the known methods. A heavy atom like oxygen, for example, it expelled as a radiant particle, might not attain sufficient velocity to ionise gases, or, even if it did, the range over which the ionisation would extend, as we know from the ionisation produced by the recoil atoms, would be extremely small. It must be a matter for comment, however, that hydrogen never appears in these changes, as, if it were produced, it would almost certainly be as easy to ascertain as helium. It has always seemed to me a possibility that some genetic connection may exist, after all, between thorium and uranium, although I have never been able to frame even a possible mode of so connecting these two elements. With a difference of atomic weight of six units, it is impossible to pass from one to the other by addition or expulsion of helium atoms alone.

Both with regard to helium and lead, the composition of radio-active minerals gave the first clue to the identity of the ultimate products. After the discovery of radio-activity and the elucidation of its nature, the fact that helium was found only in minerals containing uranium and thorium assumed a totally new interpretation, borne

out by the spectroscopic proof of the production of helium from radium by Sir William Ramsay and myself, and later from actinium, polonium, and even from uranium and thorium, all at the rates to be expected from radio-active data. The identification of the α particle with helium, after the weight of the α -particle had been shown by new physical methods to be four times that of the hydrogen atom, was accomplished by enclosing the radium emanation in a glass tube thin-walled enough to allow the α -particle to go through, but perfectly impervious to the passage of gas. In these circumstances, helium in spectroscopically detectable quantity was proved by Rutherford to make its appearance outside the tube.

Such confirmations by the spectroscope, welcome and gratifying as they are, are nevertheless in a sense subsidiary to the main problem, namely, the task of unravelling the complicated series of changes into its individual steps, and the characterisation by their radio-activity of the several intermediate members of the series, such as by the determination of their periods and the physical constants of the radiation α , β , or γ , to which they give rise. The determination of their chemical character, although equally important, was only later fully accomplished.

The Radiations.

In the successive radio-active changes, α - or β -particles are expelled, one α -particle per atom disintegrating for each change, although for the β -particles our knowledge is less exact. In some cases, certainly, although these are exceptional, β particles seem to be expelled along with α -particles. The α -particle is an atom of helium charged with two atomic charges of positive electricity, or, as we should now say, is the helium nucleus, deprived of the two electrons which are combined with it in the helium atom. The β particle is the negative electron, and when expelled with sufficiently high velocity is accompanied with γ -rays. The latter are X-rays of exceedingly short wave-length, varying from 1.3 to 0.1 Angström units. The shortest wave-length so far resolved by the crystal reflection method is 0.072 Å. in the spectrum of the γ -rays of radium-C. Ishino and Rutherford have recently concluded, however, that the main γ -radiation of radium C must have a wave-length lying between 0.02 and 0.007 Å. (*Phil. Mag.*, 1917, [vi.], xxxiii., 129; xxxiv., 153).

A connection exists between the speed of the change and the speed of the particles expelled, and the more rapid the change the faster in general and the more penetrating are the attendant α - or β -particles. In the case of the α -particle, an empirical logarithmic relation, known as the Geiger-Nuttall relation, enables us to calculate approximately the period of the changing element from the velocity or range of the α -particle, and vice versa, and by this means periods too long or too short to be directly measurable have been estimated. In the case of the β -rays, no definite quantitative law has yet been made out, but it is clear that a similar relationship must exist. One of the important corollaries is that changes much slower than the slowest known, namely, those of uranium and thorium, would probably not be detectable, as, even were α - or β -particles expelled, they would be of too low velocity probably to ionise gases or show fluorescent or photographic actions. Indeed, for mesothorium-I and actinium this appears to be the case. No detectable radiation is expelled, although the products conform to what would occur in β -ray changes. The period of both substances is long, and it is probable that the β -particle is expelled, but is undetectable by ionisation methods. For the slowest β -ray change, that of radium-D, with a period of twenty-four years, the β -radiation is of such low velocity as to be only capable of detection by special care, and is far less penetrating than average α -rays. These facts serve to show that changes may be going on in the non-radio-active elements which at present are beyond experimental means of detection.

(To be continued).

THE PREPARATION OF ORGANIC STANNO- AND STANNI-CHLORIDES.

PART II.—SALTS OF THE AROMATIC AMINES.

By J. G. F. DRUCE, B.Sc.

REDUCTION of aromatic nitro-compounds with tin or stannous chloride and hydrochloric acid in the laboratory method of preparing aromatic amines yields double tin haloids as intermediate products.

These compounds are now found to be identical with the stanno- and stanni-chlorides obtained from mixed solutions of amine hydrochloride and the tin chlorides. The double salts previously described have invariably been prepared by the latter method.

Slagle (*Am. Chem. Journ.*, 1898, xx., 633) has isolated two aniline stannochlorides, $C_6H_5.NH_2.HSnCl_3.H_2O$ and $(C_6H_5.NH_2)_2.H_2SnCl_4$, from the constituent chlorides. The former, containing a molecule of water of crystallisation, is found to be the less soluble of the two, and has been isolated pure as the first crop of crystals from solutions containing one molecular equivalent of aniline hydrochloride and of stannous chloride. The salt, $(C_6H_5.NH_2)_2.H_2SnCl_4$, sometimes crystallised from the filtrates of the above, and always resulted from solutions containing twice the above proportion of aniline. Slagle (*loc. cit.*) also states that *o*- and *p*-toluidine hydrochlorides form double salts with stannous chloride, viz., o - $C_7H_7.NH_2.HSnCl_3.H_2O$ and p - $(C_7H_7.NH_2)_2.H_2SnCl_4$. The latter has been obtained, but attempts to prepare the former have only led to the isolation of a compound identical in composition with the *p*-salt.

Stannichlorides of *o*- and *p*-toluidines have been obtained with one molecule of water of crystallisation, $(C_7H_7.NH_2)_2.H_2SnCl_6.H_2O$. They were obtained by the reduction of the nitrotoluenes with tin and hydrochloric acid, as in the preparation of aniline stannichloride from nitrobenzene (*CHEMICAL NEWS*, 1918, cxvii., 346). An *o*-toluidine salt, $3C_7H_7.NH_2.SnCl_4.3HCl.3H_2O$, was obtained from concentrated solutions of the constituent chlorides, but not by reduction of *o*-nitrotoluene.

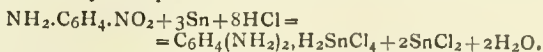
p-Toluidine stannichloride has also been prepared by adding chlorine water to solutions of the stannochloride, but the resulting product was not very pure. The *o*-toluidine salt could not be prepared in this way. The conversion of stannochloride into stanni salt by chlorination seldom gave a pure product in the case of the aromatic amine compounds.

Methylaniline formed a stannochloride,—

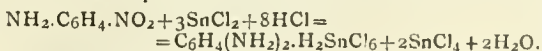


and a stannichloride, $(C_6H_5.NH.CH_3)_2.H_2SnCl_6$, when mixed with hydrochloric acid solutions of stannous and stannic chlorides in the proportions required by these formulæ. Dimethylaniline similarly gave salts $(C_6H_5.NMe_2)_2.H_2SnCl_4$ and $(C_6H_5.NMe_2)_2.H_2SnCl_6$. The stannichlorides of these two bases can also be obtained by oxidation of the stannochlorides with chlorine water, but the salts so prepared were never pure, being always more or less deeply coloured, whereas the salts derived from the mixed chlorides were always quite colourless.

The reduction of *m*- and *p*-nitroanilines with tin and hydrochloric acid has yielded the phenylene diamine stannochlorides. The course of these reductions is indicated by the equation—



When stannous chloride in hydrochloric acid was used as the reducing agent the phenylene diamine stannichlorides were produced:—



m-Dinitrobenzene has been successfully employed in the preparation of *m*-phenylene diamine compounds,

identical with those from *m*-nitroaniline. *o*-Nitroaniline did not yield the corresponding diamine salts, the crystals obtained from solutions which were expected to yield the double salts were found to be devoid of tin.

The *m*- and *p*-phenylene diamine salts prepared from the bases and hydrochloric acid solutions of the two chlorides of tin were never pure, and were always deeply coloured. Recrystallisation did not tend to give purer products in this case.

Hayes (*Journ. Am. Chem. Soc.*, 1902, xxiv., 360) describes the preparation of pyridine stannochloride, to which he assigns the formula $C_5H_5N, SnCl_2, 3HCl$. A compound having this composition has been isolated by following the procedure he recommends. This salt, like the *o*-toluidine compound $(C_7H_7NH_2)_3SnCl_7$, is an exceptional double haloid of tin and organic base.

At the end of their paper on stannisulphocyanides, Weinland and Barnes (*Zeit. Anorg. Chem.*, 1909, lxii., 250) mention that they obtained pyridine stannichloride as a precipitate on adding the base dissolved in hydrochloric acid to a solution of stannic chloride. This salt has also been prepared by the chlorination of the stannochloride.

Among the compounds of quinoline with metallic chlorides which Borsbach prepared (*Ber.*, 1890, xxiii., 431), $C_9H_7N, HSnCl_3$ and $2C_9H_7N, SnCl_4, 2HCl$ were obtained from stannous and stannic chlorides respectively. These salts have been obtained by following his method, and the stannichloride was also prepared by chlorination of the stannochloride.

By adding quinoline to solutions of various metal salts Borsbach (*loc. cit.*) obtained a pap, which, in the case of the two chlorides of tin, dissolved in hydrochloric acid, giving the stanno- and stanni-chlorides of the base. It has been found that addition of other bases (*e.g.*, aniline, pyridine, and the methylanilines) produce similar paps with stannous and stannic chloride solutions, and also when aniline was shaken up with crystalline stannic chloride, $SnCl_4, 5H_2O$, a similar product was formed.

When hydrochloric acid solutions of the amine stannochlorides were left exposed to the air, oxidation to stannichlorides slowly took place. Sometimes this was accompanied by a darkening in the colour of the solution.

Most of these double chlorides of tin and organic bases hydrolysed readily, with deposition of a white gelatinous precipitate when treated with water. Ethylamine and *m*-phenylenediamine stannochlorides, and pyridine stannichloride, for example, hydrolysed immediately when the crystals were shaken up with cold water. On the other hand, some salts like *o*-toluidine stannochloride and methylaniline stannichloride required to be boiled with water in order to cause the formation of a precipitate.

Aniline Stannochlorides.

(a) $C_6H_5NH_2, HSnCl_3, H_2O$.—This salt, containing water of crystallisation, has been prepared by dissolving 10 grms. of aniline hydrochloride in 100 cc. of dilute hydrochloric acid, and adding a solution of 17.5 grms. of crystalline stannous chloride in 120 cc. of dilute acid. On concentration the mixed solutions yielded long pale yellow prismatic crystals which dissolved slowly in cold water, but readily in hot, the solutions becoming turbid unless a few drops of hydrochloric acid were added to prevent or retard hydrolysis. When heated this salt melted at 105° with decomposition. On analysis—

0.2782 grm. gave 0.3538 grm. $AgCl$; $Cl = 31.48$ per cent.

0.4631 grm. gave 0.2069 grm. SnO_2 ; $Sn = 35.19$ per cent.

$C_6H_5NH_2, HSnCl_3, H_2O$ requires $Sn = 35.23$ and $Cl = 31.51$ per cent.

(b) $(C_6H_5NH_2)_2, H_2SnCl_4$.—Twice redistilled aniline (9.3 grms.) was added to a solution of 11.3 grms. of stannous chloride dissolved in 150 cc. of dilute hydrochloric acid. The mixture was warmed for some minutes and on cooling it deposited white pearly plates, which were

filtered off, drained at the pump, and finally dried between sheets of bibulous paper. This salt was more soluble than the above stannochloride, and was slightly hydrolysed in aqueous solution at 35°. A thick gelatinous precipitate resulted when a 5 per cent solution attained a temperature of 70°. The substance melted at 160°, and when rapidly heated began to decompose at 210°. If carefully heated above the melting-point the salt gave a white sublimate, which on examination proved to be aniline hydrochloride. The residue was very dark. When the salt was analysed—

0.5166 grm. gave 0.1743 grm. SnO_2 ; $Sn = 26.58$ per cent.

0.6315 grm. gave 0.8066 grm. $AgCl$; $Cl = 31.60$ per cent.

$(C_6H_5NH_2)_2, H_2SnCl_4$ requires $Sn = 26.52$ and $Cl = 31.58$ per cent.

Dilute hydrochloric acid solutions of this salt when exposed to the air were found to oxidise, and on concentrating the oxidised solutions crystals of anhydrous aniline stannichloride were deposited. The solutions failed to give a precipitate with mercuric chloride solution, indicating the absence of stannous salt. In one case 6 grms. of stannochloride in 100 cc. of dilute acid were completely oxidised to stannichloride on exposure for four days.

Aniline Stannichlorides, $(C_6H_5NH_2)_2, H_2SnCl_6, 3H_2O$ and $(C_6H_5NH_2)_2, H_2SnCl_6$, m.p. 293°.

These have been obtained from hydrochloric acid solutions of amine and stannic chloride, and from nitrobenzene, &c., by reduction with tin or stannous chloride in hydrochloric acid (*CHEMICAL NEWS*, 1918, cxvii., 346).

o-Toluidine Stannochloride, $(C_7H_7NH_2)_2, H_2SnCl_4$.

A hydrochloric acid solution of two molecular proportions of base and one of stannous chloride was warmed on a water-bath for an hour. Fine silky needles were deposited on cooling. These were filtered off, drained, and dried. They dissolved easily in cold water, the solution remaining clear unless boiled. When heated the salt melted at 164°. On analysis—

0.5174 grm. gave 0.1627 grm. SnO_2 ; $Sn = 24.77$ per cent.

0.2651 grm. gave 0.3202 grm. $AgCl$; $Cl = 29.89$ per cent.

$(C_7H_7NH_2)_2, H_2SnCl_4$ requires $Sn = 24.90$ and $Cl = 29.75$ per cent.

o-Toluidine Stannichlorides.

(a) $(C_7H_7NH_2)_2, H_2SnCl_6, H_2O$.—This salt has been prepared by reducing 6 grms. of *o*-nitrotoluene with 7.5 grms. of tin. Concentrated hydrochloric acid was added in small quantities until 50 cc. had been introduced into a round flask containing the mixture, which was then heated for an hour under a reflux condenser as in the case of the corresponding aniline salt (*loc. cit.*). Four grms. of *o*-toluidine were added to the reduction product to combine with the excess of stannic chloride. On heating, the very pale pink short needles which were obtained began to decompose at 210°. On analysis—

0.5063 grm. gave 0.1345 grm. SnO_2 ; $Sn = 20.92$ per cent.

0.2730 grm. gave 0.4118 grm. $AgCl$; $Cl = 37.33$ per cent.

$(C_7H_7NH_2)_2, H_2SnCl_6, H_2O$ requires $Sn = 21.01$ and $Cl = 37.64$ per cent.

(b) $(C_7H_7NH_2)_3, H_3SnCl_7, 2H_2O$.—*o*-Toluidine (4.3 grms. and stannic chloride (3.5 grms.) were dissolved together in 80 cc. of dilute hydrochloric acid, and the solution was concentrated and allowed to crystallise. The crystals were isolated and dried in air between sheets of bibulous paper, and on analysis were found to correspond with the above formula. When heated they melted at 92°.

1.1892 grm. gave 0.2491 grm. SnO_2 ; $Sn = 16.50$ per cent.

0.4065 grm. gave 0.5612 grm. $AgCl$; $Cl = 34.17$ per cent.

$(C_7H_7NH_2)_3, H_3SnCl_7, 2H_2O$ requires $Sn = 16.33$ and $Cl = 34.14$ per cent.

p-Toluidine Stannochloride, $(C_7H_7.NH_2)_2.H_2SnCl_4$.

p-Toluidine (5.35 grms.) and stannous chloride (5.65 grms.) were dissolved together in 100 cc. of dilute hydrochloric acid. The solution was concentrated, and gave nearly colourless flaky crystals which were isolated. When heated these melted at 239° . The salt dissolved in water, giving a clear solution which required heating before becoming hydrolysed. On analysis—

0.4025 grm. gave 0.1278 grm. SnO_2 ; $Sn = 25.02$ per cent.
0.2581 grm. gave 0.3081 grm. $AgCl$; $Cl = 29.57$ per cent.
 $(C_7H_7.NH_2)_2.H_2SnCl_4$ requires $Sn = 24.90$ and $Cl = 29.75$ per cent.

p-Toluidine Stannichloride, $(C_7H_7.NH_2)_2.H_2SnCl_6.H_2O$.

p-Toluidine (5.35 grms.) and stannic chloride (8.87 grms.) were dissolved together in 130 cc. of dilute hydrochloric acid by warming, and on standing overnight pale pink needle prisms separated out. These were collected, and another crop was obtained from the mother-liquor by further concentration. Both specimens melted with decomposition at 298° , and dissolved readily in cold water to a clear solution.

The stannichloride has also been obtained from a solution of 5 grms. of the stannochloride in 30 cc. of dilute hydrochloric acid by slowly running in chlorine water until the reactions for stannous tin were no longer observed. When the resulting solution was concentrated on a water-bath and then cooled, nearly colourless crystals resembling the above were obtained.

Reduction of *p*-nitrotoluene (7 grms.) with tin (19 grms.) and concentrated hydrochloric acid (80 cc.) produced a dark brown solution. The colour was considerably diminished on dilution with 150 cc. of dilute hydrochloric acid and warming with about 10 cc. of stannous chloride solution. The liquid was filtered, and 10 grms. of *p*-toluidine were added to the filtrate, which was then warmed until it became quite clear and almost colourless. On cooling pale crystals (m.p. $297-298^\circ$) of *p*-toluidine stannichloride were deposited. On analysis—

0.8265 grm. gave 0.2236 grm. SnO_2 ; $Sn = 21.31$ per cent.
0.6824 grm. gave 1.0342 grm. $AgCl$; $Cl = 37.49$ per cent.
 $(C_7H_7.NH_2)_2.H_2SnCl_6.H_2O$ requires $Sn = 21.01$ and $Cl = 37.64$ per cent.

Methylaniline Stannochloride, $(C_6H_5.NH.CH_3)_2.H_2SnCl_4$.

Redistilled methylaniline (5.35 grms.) and stannous chloride (5.65 grms.) were mixed and dissolved in 100 cc. of dilute hydrochloric acid with warming. The clear solution thus obtained deposited a mass of short stout colourless prisms. These were soluble in water, giving a clear solution which only became turbid on boiling. The salt was also soluble in cold alcohol, but only slightly so in chloroform. It melted at 106° . On analysis—

0.2549 grm. gave 0.1157 grm. SnO_2 ; $Sn = 35.75$ per cent.
0.3264 grm. gave 0.4224 grm. $AgCl$; $Cl = 32.02$ per cent.
 $C_6H_5.NH.CH_3.H_2SnCl_4$ requires $Sn = 35.63$ and $Cl = 31.93$ per cent.

Methylaniline Stannichloride, $(C_6H_5.NH.CH_3)_2.H_2SnCl_6$.

Methylaniline (5.35 grms.) and stannic chloride (8.87 grms.) were dissolved together in 120 cc. of dilute hydrochloric acid and gave, after slight concentration, colourless crystals of methylaniline stannichloride which melted with decomposition at about 251° . These crystals dissolved in water to form a clear solution which could be boiled without becoming turbid.

This compound has also been obtained by chlorinating the stannochloride, but the salt prepared by this method was not pure. On analysis—

0.4714 grm. gave 0.1306 grm. SnO_2 ; $Sn = 21.83$ per cent.
0.2072 grm. gave 0.3240 grm. $AgCl$; $Cl = 38.70$ per cent.
 $(C_6H_5.NH.CH_3)_2.H_2SnCl_6$ requires $Sn = 21.67$ and $Cl = 38.84$ per cent.

Dimethylaniline Stannochloride, $(C_6H_5.NMe_2)_2.H_2SnCl_4$.

Six grms. of dimethylaniline and 5.65 grms. of stannous chloride were dissolved together in 100 cc. of dilute hydrochloric acid. The colourless solution deposited a fine white crystalline powder when cooled. This was filtered off, drained, and dried on a porous plate. The salt melted at 87° and dissolved in cold water, but the solution became turbid in a few minutes. Addition of acids made it clear again. On analysis—

0.3026 grm. gave 0.3467 grm. $AgCl$; $Cl = 28.35$ per cent.
0.6659 grm. gave 0.1992 grm. SnO_2 ; $Sn = 23.56$ per cent.
 $(C_6H_5.NMe_2)_2.H_2SnCl_4$ requires $Sn = 23.66$ and $Cl = 28.20$ per cent.

When 6 grms. of the base and 5.65 grms. of stannous chloride were shaken up with 25 cc. of water a pap was formed similar to the one obtained with quinoline and described below. Like the latter it dissolved in dilute hydrochloric acid, and yielded crystals of the above stannochloride.

Dimethylaniline Stannichloride, $(C_6H_5.NMe_2)_2.H_2SnCl_6$.

After standing for several days the filtrate from the above stannochloride crystals no longer gave a precipitate with mercuric chloride. It was concentrated and yielded crystals of the stannichloride.

Similarly, the chlorination of a solution of 5 grms. of stannochloride in 50 cc. of dilute hydrochloric acid led to the formation of pale violet crystals of slightly impure stannichloride.

Colourless prismatic crystals were obtained from 6 grms. of dimethylaniline and 8.8 grms. of stannic chloride dissolved in 100 cc. of dilute hydrochloric acid. The salt melted at 116° , and decomposed at about 124° . It dissolved in water to a clear solution which became cloudy on boiling. On analysis—

0.4249 grm. gave 0.1131 grm. SnO_2 ; $Sn = 20.98$ per cent.
0.3222 grm. gave 0.4827 grm. $AgCl$; $Cl = 37.05$ per cent.
 $(C_6H_5.NMe_2)_2.H_2SnCl_6$ requires $Sn = 21.13$ and $Cl = 37.01$ per cent.

Attempts to Prepare *o*-Phenylenediamine Salts.

o-Nitroaniline (1.38 grms.) was reduced with tin (3.57 grms.) and hydrochloric acid (30 cc. concentrated acid diluted with 20 cc. of water). The clear solution deposited very pale yellow radiating transparent prisms, which were isolated. When analysed these crystals were found to be devoid of tin, and the chlorine found was approximately that required for *o*-phenylenediamine hydrochloride:—

0.3314 grm. gave 0.5255 grm. $AgCl$; $Cl = 39.24$ per cent.
 $C_6H_4(NH_2)_2.HCl$ requires $Cl = 39.15$ per cent.

The mother-liquor failed to yield crystals of a double chloride after concentration, but assumed a brown colour which became deeper as the evaporation proceeded. Analyses of the substance finally deposited were not concordant, and did not point to any definite compound.

Reduction of *o*-nitroaniline with stannous chloride similarly did not lead to the isolation of a crystalline stannichloride.

m-Phenylenediamine Stannochloride, $C_6H_4<\begin{smallmatrix} NH_2, H_2SnCl_3 \\ NH_2, H_2SnCl_3 \end{smallmatrix}$.

This salt has been prepared from *m*-nitroaniline and also from *m*-dinitrobenzene.

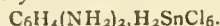
m-Nitroaniline (2 grms.) and tin (5 grms.) were put in a round flask fitted with an air condenser. Thirty cc. of concentrated hydrochloric acid and 20 cc. of water were added, and the mixture was gently heated until all the tin had disappeared and the solution was colourless. This was then transferred to a basin to cool, when it deposited a mass of prisms about 3 cm. in length. These dissolved in cold water, but the solution became cloudy as a result of hydrolysis. Solutions of the salt in dilute acid gave a precipitate with aqueous mercuric chloride, the precipitate

darkened on warming. Iodine solutions were decolorised by the salt in dilute hydrochloric acid. The precipitate with hydrogen sulphide was dark brown. These reactions are typically those of a stannous compound. The salt melted at 128° .

For the reduction of *m*-dinitrobenzene with tin, 3.76 grms. of the former were mixed with 14.4 grms. of the metal, and 60 cc. of concentrated hydrochloric acid diluted with 20 cc. of water were added. On gently warming a sudden reaction set in. The resulting solution was quite colourless, and on cooling it deposited a mass of colourless needle crystals which were isolated. They were found to possess properties identical with the salt obtained from *m*-nitroaniline. On analysis—

0.5174 grm. gave 0.2753 grm. SnO_2 ; Sn = 41.92 per cent.
0.2439 grm. gave 0.3762 grm. AgCl; Cl = 38.18 per cent.
 $\text{C}_6\text{H}_4(\text{NH}_2)_2 \cdot 2\text{HSnCl}_3$ requires Sn = 41.85 and Cl = 37.97 per cent.

m-Phenylenediamine Stannichloride,



m-Nitroaniline (2.56 grms.) and crystalline stannous chloride (10.5 grms.) were dissolved by warming in 120 cc. of dilute hydrochloric acid. At first the liquid was very cloudy, but it gradually became clear and colourless. (When insufficient stannous chloride was employed a pink solution was produced). On cooling, almost colourless crystals of *m*-phenylenediamine stannichloride were obtained. These dissolved easily in cold water to a clear solution which was not appreciably hydrolysed unless the solution was almost raised to the boiling-point. The solutions gave no precipitate with mercuric chloride, indicating the absence of stannous salt. When heated the crystals began to darken and decompose at about 265° .

When 1.68 grms. of *m*-dinitrobenzene were reduced with 13.56 grms. of stannous chloride in 150 cc. of dilute hydrochloric acid by warming and the resulting clear solution was concentrated and cooled, crystals of the stannichloride were deposited.

On exposure to air dilute acid solutions of *m*-phenylenediamine stannochloride oxidised, and on concentration frequently deposited crystals of the stannichloride, which, however, were seldom pure. The pure salt was analysed as follows:—

0.4762 grm. gave 0.1606 grm. SnO_2 ; Sn = 26.56 per cent.
0.4511 grm. gave 0.8767 grm. AgCl; Cl = 48.07 per cent.
 $\text{C}_6\text{H}_4(\text{NH}_2)_2 \cdot \text{H}_2\text{SnCl}_6$ requires Sn = 26.88 and Cl = 48.18 per cent.

p-Phenylenediamine Stannochloride, $\text{C}_6\text{H}_4(\text{NH}_2)_2 \cdot \text{H}_2\text{SnCl}_4$.

This salt was prepared from *p*-nitroaniline (1.38 grm.) and tin (3.58 grms.) in the same way as the *m*-phenylenediamine salt.

A mass of feathery crystals separated out as the solution cooled, but they soon changed into more compact masses, becoming white and opaque. They were filtered off, drained, and dried between sheets of bibulous paper. They dissolved in cold water, but the solution hydrolysed on warming. The salt melted with decomposition at 270° . On analysis—

0.5984 grm. gave 0.2425 grm. SnO_2 ; Sn = 31.92 per cent.
0.3707 grm. gave 0.5734 grm. AgCl; Cl = 38.29 per cent.
 $\text{C}_6\text{H}_4(\text{NH}_2)_2 \cdot \text{H}_2\text{SnCl}_4$ requires Sn = 32.06 and Cl = 38.26 per cent.

p-Phenylenediamine Stannichloride, $\text{C}_6\text{H}_4(\text{NH}_2)_2 \cdot \text{H}_2\text{SnCl}_6$.

The mother liquors obtained in the preparation of the above stannochloride, on long standing, deposited crystals, which no longer gave a precipitate with mercuric chloride in solution, and which, on treatment in solution with hydrogen sulphide, gave a yellow precipitate of stannic sulphide.

The stannichloride was prepared in larger quantity from 1.38 grms. of *p*-nitroaniline and 6.78 grms. of stannous chloride by warming with 80 cc. of dilute hydrochloric acid. After one and a half hours the solution was quite clear and colourless, and on cooling crystals separated. These were filtered off, drained, and dried on a porous plate. They dissolved in cold water without apparent hydrolysis, but on boiling a precipitate was obtained. No precipitate resulted on addition of mercuric chloride to an acid solution. The crystals melted with decomposition at 230° . On analysis—

0.7652 grm. gave 0.2589 grm. SnO_2 ; Sn = 26.65 per cent.
0.1728 grm. gave 0.3352 grm. AgCl; Cl = 48.02 per cent.
 $\text{C}_6\text{H}_4(\text{NH}_2)_2 \cdot \text{H}_2\text{SnCl}_6$ requires Sn = 26.88 and Cl = 48.18 per cent.

Pyridine Stannochloride, $\text{C}_5\text{H}_5\text{N} \cdot \text{SnCl}_2 \cdot 3\text{HCl}$.

Pyridine (3.16 grms.) was dissolved in 30 cc. of dilute hydrochloric acid. When cold, this solution was treated with a cooled solution of 4.52 grms. of stannous chloride in 40 cc. of dilute hydrochloric acid. The latter solution was slowly added with stirring. Finally a white crystalline precipitate began to form. After twelve hours this was filtered off, dried, and examined. It melted at 115° . On analysis—

0.4056 grm. gave 0.1601 grm. SnO_2 ; Sn = 31.10 per cent.
0.1774 grm. gave 0.3376 grm. AgCl; Cl = 47.05 per cent.
 $\text{C}_5\text{H}_5\text{N} \cdot \text{SnCl}_2 \cdot 3\text{HCl}$ requires Sn = 31.47 and Cl = 46.75 per cent.

Pyridine Stannichloride, $(\text{C}_5\text{H}_5\text{N})_2 \cdot \text{H}_2\text{SnCl}_6$.

Pyridine (3.16 grms.) was added with stirring to stannic chloride (7.02 grms.) dissolved in 80 cc. of dilute hydrochloric acid. Colourless octahedral crystals of pyridine stannichloride, which melted at 305° , separated out on standing overnight. The salt was soluble in water, but the clear solution became very turbid on heating.

Another specimen was prepared by dissolving 6 grms. of the stannochloride in 60 cc. of dilute acid and passing a slow stream of chlorine through the liquid until the latter no longer gave a precipitate with mercuric chloride. Two grms. of pyridine were added to convert all the tin present into stannichloride, and the solution was slightly concentrated on a water-bath. It deposited crystals, having properties identical with those obtained above. On analysis—

0.7539 grm. gave 0.2361 grm. SnO_2 ; Sn = 24.67 per cent.
0.2755 grm. gave 0.4838 grm. AgCl; Cl = 43.44 per cent.
 $(\text{C}_5\text{H}_5\text{N})_2 \cdot \text{H}_2\text{SnCl}_6$ requires Sn = 24.45 and Cl = 43.81 per cent.

Quinoline Stannochloride, $\text{C}_9\text{H}_7\text{N} \cdot \text{HSnCl}_3$.

When quinoline was added drop by drop to clear solutions of stannous chloride dissolved in alcohol or in dilute acid a thick white pap was produced. This pap dissolved on adding dilute hydrochloric acid and warming, and the clear solution thus obtained deposited a mass of fine white needle crystals of the stannochloride. These were collected and dried. On heating they melted at 127° .

Quinoline stannochloride was also obtained direct from a solution of quinoline (5 grms.) in dilute hydrochloric acid (50 cc.), which was mixed with a solution of 9 grms. of stannous chloride in 60 cc. of dilute acid. The salt which crystallised out after concentration had the same melting-point and gave similar analytical results to the specimen prepared by Borsbach's method. On analysis—

0.4055 grm. gave 0.1728 grm. SnO_2 ; Sn = 33.56 per cent.
0.1454 grm. gave 0.1767 grm. AgCl; Cl = 30.04 per cent.
 $\text{C}_9\text{H}_7\text{N} \cdot \text{HSnCl}_3$ requires Sn = 33.60 and Cl = 29.96 per cent.

Quinoline Stannichloride, $(C_9H_7N)_2, H_2SnCl_6$.

Stannic chloride (7 grms.) and quinoline (5 grms.) were dissolved together in 100 cc. of dilute hydrochloric acid by warming. On cooling, small white granular crystals separated and were isolated.

Quinoline stannichloride did not dissolve readily in cold water, and on warming the solution was very rapidly hydrolysed. It did not dissolve very well in cold dilute acids, but was more soluble when warm solutions were employed. The solid when heated melted at 250° (a second crop from the mother liquors melted at 258°). Borsbach (*loc. cit.*) states that the substance remained solid up to 240° .

When quinoline was added drop by drop to a solution of stannic chloride in dilute acid a fine white crystalline powder separated out. On examination it was found to be identical with the product obtained above.

It has also been possible to prepare quinoline stannichloride by dissolving the stannochloride (6 grms.) in 100 cc. of dilute hydrochloric acid and slowly passing in chlorine for four hours, after which the solution no longer contained any stannous salt. It was warmed on a water-bath for half an hour, a gm. of free base was added, and when cold, crystals which were similar in appearance to those above, and identical with them in behaviour and composition, separated out. On analysis—

0.4714 gm. gave 0.1187 gm. SnO_2 ; $Sn = 19.92$ per cent.

0.1011 gm. gave 0.1462 gm. $AgCl$; $Cl = 35.73$ per cent.

$(C_9H_7N)_2, H_2SnCl_6$ requires $Sn = 20.05$ and $Cl = 35.95$ per cent.

THE INFLUENCE OF CATALYSTS ON THE CHLORINATION OF HYDROCARBONS.

By V. R. KOKATNUR.

THE object of this paper is to show the contrasting action of light and of catalysts on the chlorination of hydrocarbons.

It is well known that chlorine acts progressively on aliphatic hydrocarbons in the presence of light, giving products of the nature of CH_3Cl , CH_2Cl_2 , $CHCl_3$, and CCl_4 , as in the chlorination of methane. On the aromatic hydrocarbons, on the other hand, it acts, under the same conditions, additively in the ring or substitutively in the side chain. Substitution in the ring requires the use of strong halogen carriers.

It is also known that halogen carriers can be employed in the chlorination of aliphatic hydrocarbons, giving the same ultimate products as in the chlorination under the influence of light. Halogen carriers seem to have a selective action in the substitution of aromatic hydrocarbons in preference to aliphatic. Thus in the chlorination of toluene in the presence of catalysts at a low temperature substitution is restricted to the ring, without in the least affecting the side chain. At a higher temperature, however, substitution takes place in the side chain in preference to the ring. It is likely that even at a low temperature, when the substitution has gone as far as pentachlorotoluene, the side chain will then be attacked.

Regnault (*Ann.* 1849, xxxiii., 332) demonstrated that chlorine acts progressively on methane in the presence of light, forming CH_3Cl , CH_2Cl_2 , $CHCl_3$, add CCl_4 , all of which can be isolated.

Bedford (U.S.P. 1,245,553, Nov. 6, 1917) claims to have obtained $CHCl_3$, CH_2Cl_2 , CH_3Cl , and CCl_4 , either singly or collectively, according to the control of conditions. He made methane and chlorine to react in the presence of ice and actinic light. Masland and Sparre (U.S.P. 1,148,259, July 27, 1915) claim to obtain mono-, di-, tri-, or tetrachlorinated hydrocarbons according to conditions in the chlorination of petroleum under the influence of light. Brooks, Essex, and Smith (U.S.P.

1,191,916, July 18, 1916) make similar claims in the chlorination of gasoline. Blanc (U.S.P. 1,248,065, Nov. 27, 1917) uses both carriers and actinic light in the chlorination of petroleum and claims to have obtained similar results.

Colin (U.S.P. 427,744, May 13, 1890) made attempts to burn methane in chlorine by electric sparks of proper tension, and separate the reaction mixture by fractionation, but his attempt failed completely.

Pfeifer and Szaroasy (D. Ann. P. 12,058, Sept. 25, 1911) proposed to expose a mixture of methane and chlorine to the action of silent electric discharge.

In 1879 Mallet (U.S.P. 220,397, Oct. 7, 1879) proposed to pass the mixture of chlorine and methane through an inert but porous material, like carbon, using it as a halogen carrier instead of light. J. Mackaye (U.S.P. 880,900, March 3, 1908, and 1,009,428, Nov. 21, 1911) working under similar conditions, claims to have obtained the intermediate products like $CHCl_3$.

Meyer (*Ber.*, 1891, xxiv., 4248) showed that ethylenedibromide can be prepared from ethylbromide, by heating it with bromine in the presence of iron wire, in a sealed tube.

Burgoin (*Compt. Rend.*, 1875, xxix., 325) obtained pentabromoethane by heating tetrabromoethane with 15.6 per cent bromine in a sealed tube for two days.

In 1893 Phillips (*Am. Chem. Journ.*, 1893, xvi., 362) reported that in the chlorination of methane under the influence of carriers, the tendency was to form the first and the last substitution products at the sacrifice of the intermediate ones. Thus, he says, very little or no CH_2Cl_2 and $CHCl_3$ were formed in the reaction.

Tokozcko (*Abhandl. Trakann. Wies.*, 1912; *Journ. Soc. Chem. Ind.*, 1913, xxxii., 742) obtained results identical with those of Phillips. Monneyrat (*Compt. Rend.*, 1896, cxxvi., 1805) showed that chlorination of tetrachloroethane in the presence of aluminium chloride gave hexachloroethane only, without producing any pentachloroethane.

General Method.

A known amount of acetylene tetrachloride was placed in a flask with or without a reflux condenser. The catalyst was either dissolved or suspended in the liquid. A known amount of chlorine was passed through the solution slowly. The reaction product was first washed with dil. sodium hydroxide solution and then with water to remove all hydrochloric acid and free chlorine. It was then dried over calcium chloride and distilled. The fraction passing over below 150° was regarded as acetylene tetrachloride, b.p. 145 to 148° . The fraction above 150 to 170° was freed from hexachloroethane by either cooling the liquid and thus crystallising out the solid, or by successive distillation whereby hexachloroethane remained in the distilling flask. This hexachloroethane-free liquid was redistilled to find out whether it was acetylene tetrachloride or pentachloroethane, b.p. 157 — 160° .

Experimental.

1. 25 grms. of specially prepared vegetable charcoal previously tested as a catalyst, was suspended in 100 cc. of acetylene tetrachloride, $C_2H_2Cl_4$; 50 grms. of chlorine was passed through this solution in seven hours at room temperature. (Vegetable charcoal from the market was first treated with conc. HCl and then dried in an atmosphere of chlorine for about three hours at a temp. of 600 — 700°). The reaction produced was washed, dried, and distilled. The first fraction, below 150° , amounted to 60 cc. and consisted of acetylene tetrachloride. The second fraction, between 150° and 170° , amounted to 30 cc. and was mostly hexachloroethane mixed with small amounts of acetylene tetrachloride.

2. 50 grms. of animal charcoal was suspended in 200 cc. of acetylene tetrachloride and 180 grms. chlorine was passed through in seventeen hours at a temperature between 60° and 70° . The reaction product was washed,

dried, and distilled as before. The first fraction, below 150° , amounted to 140 cc. and was found to be acetylene tetrachloride. The second fraction, between 150° and 170° , amounted to 45 cc. and was mostly hexachloroethane mixed with small amounts of acetylene tetrachloride.

3. The results were the same as in the second experiment, except that 75 grms. of hexachloroethane was added to see whether its presence would tend to make the reaction stop at the pentachloroethane stage. But results were obtained similar to those of Expt. 2.

4. 200 grms. of iron was suspended in 200 cc. of acetylene tetrachloride and 140 grms. of chlorine was passed through in twenty-three hours at room temperature. The reaction produced was washed, dried, and distilled. The first fraction, below 15° , amounted to 140 cc. and was acetylene tetrachloride. The second fraction, between 150° and 170° , totalled 50 cc. and was mostly hexachloroethane.

5. Duplicating (4), except at a temperature of 70 to 80° . The results were similar except that the yield of hexachloroethane was greater.

6. To 200 cc. of acetylene tetrachloride 200 grms. of bleaching powder and 200 cc. of water were added, and the mixture was heated on the water bath for several hours. The insoluble liquid formed was separated and distilled. There was a considerable loss, as some of the liquid was absorbed in the lime and could not be separated. The first fraction consisted of trichloroethylene, unsymmetrical and symmetrical tetrachloroethane. The second fraction was pure hexachloroethane.

7. Duplicating (6), but at a temperature of 130 to 140° . The results were similar but larger yields of each were obtained.

8. To 200 cc. of acetylene tetrachloride, 112 grms. of anhydrous aluminium chloride was added and the mixture was heated for three hours at a temperature of 60 to 70° . The reaction produced was treated with water, the oily liquid separated, dried, and distilled. The first fraction, below 150° , amounted to 145 cc. and was found to be a mixture of unsymmetrical and symmetrical tetrachloroethane. The second fraction, below 170° , was pure hexachloroethane.

9. Duplicating (8), but with 30 grms. of aluminium chloride and heating on the water bath for several hours. Larger yields of unsymmetrical tetrachloroethane and hexachloroethane were obtained.

10. Duplicating (9), but with 20 grms. of aluminium chloride and passing chlorine at room temperature. Only 80 cc. was unchanged. The rest was hexachloroethane.

Discussion.

These experiments show the influence of catalysts on the chlorination of hydrocarbons. Under their influence the chlorination is carried to the end-point without stopping at intermediate points.

Whether the production of hexachloroethane in the chlorination of acetylene tetrachloride (symmetrical tetrachloroethane) should be accounted for by the influence of catalysts or by the symmetrical structure of the compound, it is difficult to say. It is true that the two hydrogen atoms in the molecule of acetylene tetrachloride have the same value, being symmetrically placed with regard to the whole molecule; hence there is no reason why one atom should be substituted and the other not. Thus it is conceivable that both hydrogen atoms are substituted simultaneously, giving hexachloroethane as the final product. Further light on this point can only be thrown when unsymmetrical tetrachloroethane is chlorinated. If it gives pentachloroethane, then it may be argued that the symmetrical nature of tetrachloroethane is the cause of not obtaining pentachloroethane as an intermediate product.

It is significant to note that the same symmetrical tetrachloroethane gives pentachloroethane when the chlorination is carried on in the presence of actinic light. This may perhaps mean that light changes the symmetrical

nature of the compound while chlorinating, thus making it possible to obtain pentachloroethane; or it may mean that it dissociates chlorine into bi-atomic mono-molecular units, which acting on tetrachloroethane gives pentachloroethane. Conversely it must be assumed, however, that the catalysts tend to associate the chlorine molecules into bi-molecules. Hence chlorination in the presence of catalysts may be called a bi-molecular reaction, while it is a mono-molecular reaction in the presence of actinic light. Thus it might be expected that methane, after chlorination, would give CH_2Cl_2 and CCl_4 , though Phillips claims to have obtained CH_3Cl and CCl_4 .

This is an inviting field and more definite work must be done before any hypothesis is proposed.—*The Journal of the American Chemical Society*, xli., No. 1.

THE FRUIT OF THE *PYRUS AMERICANA*.

By VERNON C. SHIPPEL.

THE fruit of the *Pyrus Americana*, or mountain ash, was sent us from Victor, Montana. It had been dried for some time, but still retained a fresh, bright-red appearance. The average weight of each dried berry was 0.1668 of a gm. Three portions were ashed, and the amount of the ash remained fairly constant, between 4 and 5 per cent.

The Sugars.

We used the Maxwell extraction apparatus. A hundred grms. of the fruit was placed in flask A and treated with alcohol for four weeks. Both flasks are partly filled with alcohol, and the siphon is filled with the same liquid. Both flasks are heated on the water-bath. The vapour formed in flask B will force its way through the short siphon to flask A, and it will be condensed by the condenser above. The vapour from flask A will also be condensed and return to the same flask. This soon lowers the level of the liquid in flask B and raises it in flask A, and starts the action of the siphon which carries the oil laden alcohol from flask A to B. Here the alcohol vapourises, leaving its burden of oil in flask B and returns in the form of vapour to flask A to be condensed and to begin anew its cycle of extracting, transporting, and depositing another portion of oil. We have found the apparatus economical of both time and material.

After the four weeks' use of alcohol, we used water as the solvent for two weeks longer, until the liquid which came over into flask B showed no trace of sugar. The berries were then removed from the extraction apparatus, thoroughly dried and weighed. The loss of weight, 32 per cent, approximated the percentage of sugar.

The alcoholic and water extractions were united, evaporated to a small volume, and then diluted with water to a litre. A portion of this solution was treated with bone-black, but it did not become entirely colourless. A cubic centimetre was added to 50 cc. water, and treated with Fehling's solution of such a strength that 1 cc. corresponded to 0.005 gm. sugar. The sugar solution was kept boiling during the addition of Fehling's solution. Small portions were filtered from time to time to determine when the end of the reaction was reached. Several fairly concordant determinations were made which indicated 34 per cent of sugar.

Some of the sugar was tested with phenyl hydrazine hydrochloride, and the time of osazone formation, one and a half minutes, indicated that the sugar was fructose. Search was made for other varieties, but none other could be detected.

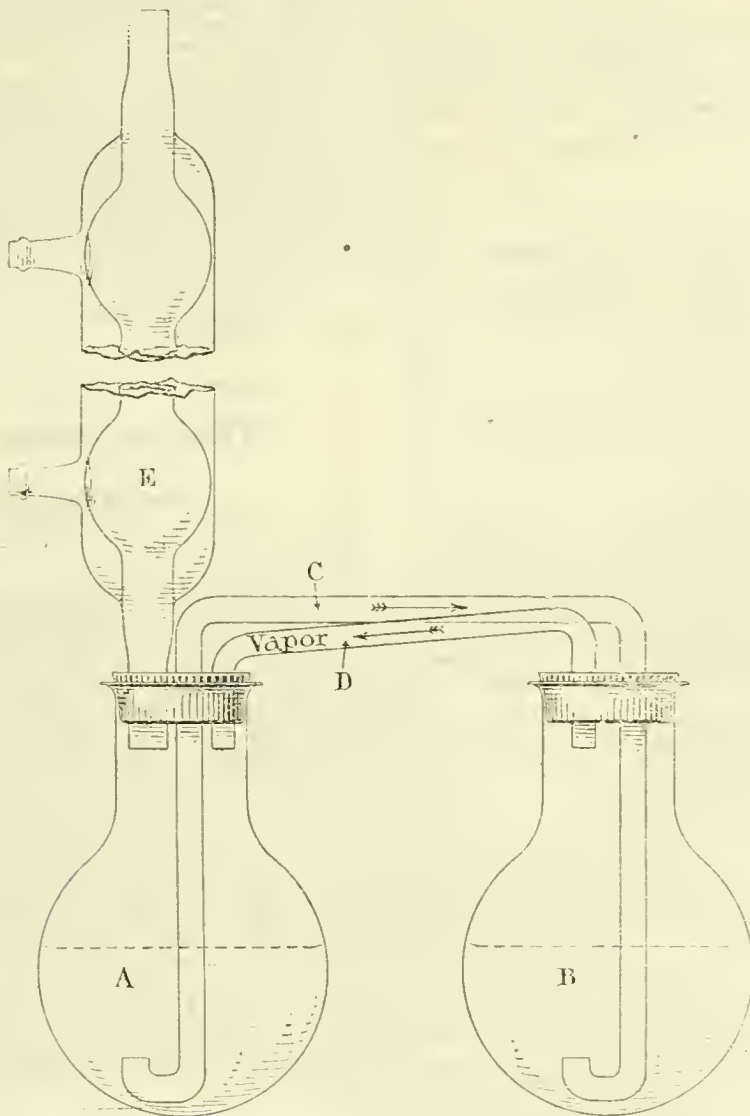
The Oils.

The dried residues from the sugar extraction were placed in the same extraction apparatus and treated with ether for five weeks, when all oil seemed to be removed. It was

found when the residues were again dried that they had not lost much in weight. The oil was separated from the ether by heating in a small flask, and it seemed difficult to remove the last traces of ether. The oils were decidedly coloured, and again ether was added and they were treated with bone-black on a warm water-bath for several hours. When filtered the solution was perfectly clear. There seemed to be two oils, one lighter and floating on top. At this point the oils were set away for the summer, and in

The Acids.

Tests for the more common organic acids revealed traces of tartaric and citric acids, but malic acid predominated. It was determined as follows:—Two and a half grms. of the fruit were placed in a flask fitted with a return condenser, the fruit covered with distilled water and boiled for several hours. The extract was titrated with tenth-normal caustic soda solution, and found to contain 2.34 per cent of malic acid.



EXTRACTION APPARATUS. (Designed by Harold Maxwell).

the fall it was found that one oil had solidified and had changed to a yellowish colour. In the attempt to determine the specific gravity of the liquid oil, some ether was still found to be present in it. This portion was then spread out on a watch-glass and soon the ether disappeared and the oil became a semi-solid. The other portion seemed to be a gum rather than an oil. The two portions weighed 3 grms. or 3 per cent of the original fruit. The quantities proved too small to determine their characteristics.

The Nitrogen.

The total nitrogen was determined by the Kjeldahl-Gunning method and 0.57 per cent was found.

The Ash.

Three separate portions of fruit, between 2 and 3 grms. in each portion, were ashed in a platinum dish, from which the various constituents were determined. The per cent of ash was as follows:—(1) 4.81 per cent; (2) 5.21 per cent; (3) 5.02 per cent. The average was 5.01 per cent

	Per cent.
SiO ₂	1.68
Fe ₂ O ₃ and Al ₂ O ₃	0.91
CaO	3.36
MgO	5.82
K ₂ O	0.55
Na ₂ O	4.96
P ₂ O ₅	29.39

There was carbon dioxide in the ash which we did not determine quantitatively, but which might be computed from the foregoing results. The methods employed in determining the various constituents of the ash were taken from Knight's "Quantitative Analysis," Revised Edition.

Our thanks are due to Dr. Nicholas Knight for his helpfulness in this work.

Cornell College, January 18, 1919.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, February 6, 1919.

Sir J. J. THOMSON, President, in the Chair.

THE following papers were read:—

"Note on the Elasticity of Metals as affected by Temperature." By A. MALLOCK, F.R.S.

The present note is an account of some preliminary experiments on the variations with temperature of Young's Modulus for fifteen selected metals. The choice was influenced largely by the ease with which specimens could be procured. No alloys are included. The metals chosen were rhodium, platinum, iron, palladium, nickel, copper, gold, silver, magnesium, aluminium, zinc, lead, cadmium, bismuth, and tin.

The procedure was to determine the frequency of the vibrations of a stiff rod carried at its lower end by a small thin plate of the material to be tested, the other end of the plate being clamped to a fixed support. The plate and its support could be immersed in fluid of any desired temperature without wetting the rod and in any way interfering with the mounting. The temperatures employed were those of liquid air, 0° Centigrade, ordinary temperature (10–15°) and as near 100° C. as was practicable. The measured frequencies of vibration at these temperatures furnished the necessary data for determining the changes in Young's Modulus.

The results showed that the more infusible the metal the less the Modulus was affected for a given change of temperature, and this suggested that there might be a real connection between the variation of the Modulus (M) and the melting point θ_M in Absolute temperature.

A diagram is given comparing the experimental results with what they would have been had the relation $dM/d\theta = \theta_M$ been true. If this relation holds and θ_1 , θ_2 are two temperatures for which the Moduli are M_1 , M_2 , then would $M_1/M_2 = \theta_M - \theta_1 / \theta_M - \theta_2$, and if θ_1 is Absolute zero and $\theta_2 = 0^\circ$ C., so that in this case $M_1/M_2 =$ Melting point Absolute for any two temperatures Melting Point Centigrade differing by 270° C.

The experimental results show a distinct resemblance to those obtained on this supposition.

"Vibration and Strength of Struts and Continuous Beams under End Thrusts." By W. L. COWLEY and H. LEVY.

In a previous communication, "The Critical Loading of

Struts and Structures," the authors investigated the stability of a strut under end thrust and simply supported at a number of intermediate points. The method of analysis has been extended in the present paper to include the more general problem of the vibration of such a system when the lateral load is periodic and the supports are assumed in a state of vibration. The flexural rigidity and the end thrust, constant along each bay, are taken for further generality to vary from bay to bay. These conditions correspond closely with those originated in a wing spar of an aeroplane when in flight and influenced by engine throbbing.

A very general form of the equation of three moments is derived, and the conditions for resonance and crippling expressed in a convenient determinantal form.

The general case where the end thrust, the flexural rigidity, and the mass per unit length, vary between the supports according to any assumed law is discussed, and the method of solution illustrated in the particular case of the crippling of a strut of variable flexural rigidity. The result is expressed in a form extremely convenient for graphical treatment.

"A New Method for the Absolute Determination of Frequency." By A. DEY.

NOTICES OF BOOKS.

The Manufacture of Intermediate Products for Dyes. By JOHN CANNELL CAIN, D.Sc. (Manchester). London: Macmillan and Co., Ltd. 1918. Pp. xi+263. Price 10s. net.

CHEMISTS have recently been very frequently called upon to supply information relating to the manufacture and properties of intermediate products for dyes, and no doubt such demands upon their knowledge will continue to increase as the British dye industry becomes more firmly established and flourishing. But it has often been a matter of considerable difficulty to supply manufacturers with exactly the details they require. Descriptions of processes are scattered throughout literature which is often not readily accessible, and it has meant the expenditure of much time in going through patent specifications, &c., in order to get the most recent and reliable data. The author's aim in preparing this book has been to bring together all such details of processes of manufacture actually employed, so that his readers will have no need to refer to the original descriptions, and this aim has been admirably fulfilled. The chief operations which are constantly employed, including chlorination, nitration, and sulphonitration, for example, are described in full, and the actual arrangement of work is given, with all essential details as to quantities employed, yields, physical constants, &c. The most important compounds have been judiciously selected for fullest description, and in some cases the author has added notes on the results of his own experience.

Annuaire pour l'An 1919 publié par le Bureau des Longitudes. ("Annual for 1919 published by the Bureau des Longitudes"). Paris: Gauthier-Villars et Cie. Pp. viii+680. Price 3 francs net.

THE current number of this annual contains the usual astronomical data giving the relative positions of the sun, earth, moon, planets, and stars for every day in the year, and also copious statistics relating to the population of the chief towns in France, &c. It contains interest and annuity tables, and although some changes in detail have been made in this year's issue the Annual will certainly be no less useful than heretofore, particularly to astronomers and statisticians.

BOOKS RECEIVED.

- "Recent Advances in Physical and Inorganic Chemistry." By ALFRED W. STEWART, D.Sc. With an Introduction by Sir WILLIAM RAMSAY, K.C.B., F.R.S. Third Edition. Pp. xv+284. Price 12s. 6d. net. London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. 1919.
- "The Atomic Weights of Boron and Fluorine." By EDGAR F. SMITH and WALTER R. VAN HAAGEN. Pp. iv+65. Washington: The Carnegie Institution. 1918.
- "Introduction à la Chimie Générale." By H. COPAUX. Pp. 212. Paris: Gauthier-Villars. 1919. Price 6 francs.
- "Trattato di Chimica Generale ed Applicata all' Industria." Vol. I. Chimica Inorganica. Parte Seconda. By Dott. ETTORE MOLINARI. Quarta Edizione, rivedita ed ampliata. Pp. 630. Milano: Ulrico Hoepli. 1919. Price L. 26.
- "Riso e Vitamine." By Prof. ICILIO GUARESCHI. Estratto dal Supplemento Annuale all' Enciclopedia di Chimica o Archivio di Chimica Scientifica e industriale. Vol. XXXIV. 1918. Pp. 143.
- "Imperial University of Tokio—Calendar, 1917-1918." Tokyo: The University.

CORRESPONDENCE.

IMPORT RESTRICTIONS.

To the Editor of the Chemical News.

SIR,—We understand that the policy to be adopted in regard to the continuation of restrictions on Imports is receiving the consideration of the War Cabinet. The Federation desires to press most strongly on the Government the absolute necessity of not allowing products which compete with those of any Industry in this country to be imported and sold at prices with which existing conditions make it impossible for the home industry to compete, until that industry has had a reasonable opportunity of converting from a war to a peace footing. Unless this course is adopted the resumption of normal industrial activity in this country will be gravely prejudiced, and the effect upon employment must be most serious in the present condition of industrial unrest.

The Federation realises that pressure may be being brought to bear upon the British Government by Foreign Governments who desire to import into this country, but such considerations appear to them to be infinitely less important than those to which reference has been made above.

In any case they would urge that no relaxation of import restrictions should be made in deference to the representations of a foreign Government without securing from that Government a substantial *quid pro quo*, and that in any such case the relative value of the concession which is being made to the Foreign Government and of the benefit to be received in return should be most carefully weighed.

Finally, I am to urge that no decision should be taken on this most important question without the fullest consultation with representatives of the industry of the country, and to say that we should be most willing to place our organisation at the service of the Government to advise them, should they so desire. I am to point out further that the decision of the questions which arise in connection with the raising of restrictions and granting of licences often involves very minute enquiries into the available and potential supplies of small articles. These enquiries can most satisfactorily be made through an organisation such as ours, which comprises manufacturers

in every branch of industry and has collected very full statistics as to the products of the various industries, and we have already been able to render considerable assistance to the Government in dealing with questions of this kind referred to us by the Department of Import Restrictions.—I am, &c.,

V. CAILLARD,

President, Federation of British Industries.

39, St. James's Street, S.W. 1.

OBITUARY.

PROF. GEORGE CAREY FOSTER.

WE regret to have to announce that Prof. George Carey Foster, B.A., LL.D., D.Sc., F.C.S., F.R.S., died on Sunday, February 9, at his residence at Rickmansworth.

Prof. Carey Foster was the only son of the late George Foster, of Sabden, in Lancashire, where he was born in 1835. He was educated at University College, London, and studied also at the Universities of Ghent, Heidelberg, and Paris. In 1862 he was appointed Professor of Natural Philosophy in Anderson's College, Glasgow, and three years later he became Professor of Physics at University College, London, which appointment he held until 1898. From 1900 until his retirement in 1904 he was Principal of the College. He was a highly successful teacher of physics and the Physical Laboratory at University College was the first in which practical instruction in the subject was given to students. Prof. Foster's text books also were much valued by students, for he had a marked gift for clear explanation, and he was a popular principal, showing great administrative gifts. He was one of the founders of the Physical Society of London, and was President from 1877 to 1879. He was President of the Society of Telegraphic Engineers (now the Institution of Electrical Engineers) in 1887, and held the office of General Treasurer to the British Association for the Advancement of Science from 1898 to 1904. Prof. Carey Foster was elected a Fellow of the Royal Society in 1869 and was Vice-President in 1891-93 and again in 1902-3.

MISCELLANEOUS.

Royal Institution.—Sir Oliver Lodge will deliver the Friday Evening Discourse at the Royal Institution on February 28, at 5.30 p.m., on "Ether Matter." Owing to indisposition Prof. J. A. McClelland will be unable to deliver his Discourse on "Nuclei and Ions" as announced.

Willow Calf Leather.—As a preservative, leather treated with an ammoniacal vegetable oil emulsion if already waxed will be darkened somewhat, but is both renovated and capable for further use.—J. C. THOMLINSON, B.Sc.

Action of Cyanide Solution in Dissolving Gold.—A valuable paper by Mr. T. B. Crowe, E.M., has appeared in the *Transactions of the American Institute M.E.* (Aug., 1918, p. 1279), "On the Action of Cyanide Solution in Dissolving Gold, and the Effect of Zinc in Recovering the Gold from such Solutions." Experiment and practical work combined have shown that the solution of gold by cyanide of potassium is essentially an oxidation process. In vacuo the action of KCy upon gold practically ceased; on the other hand, in treating cyanide solutions for the recovery of gold the absence of air is a great advantage. These two reactions have been introduced into practice in the mines and have resulted in a considerable saving both in cyanide of potassium and zinc, with increased working efficiency.

Emulsions and Colloidal Solutions.—An emulsion can be remade with vegetable oil in aqueous ammoniacal emulsions, after settling, by adding coal-tar naphtha, by placing a string thoroughly fixed by the cork in the bottle and shaking, probably colloidal solution occurring at the same time.—J. C. THOMLINSON, B.Sc.

Determination of Saccharine in Tabloids.—A. Bonis.—Tabloids of saccharine are composed either of saccharine or of sodium saccharinate, or of a mixture of these two substances, generally with the addition of sodium bicarbonate; the simultaneous presence of saccharine and saccharinate results from the partial action of saccharine on sodium bicarbonate either in the course of manufacture or by the slow action of moisture. Lactose is sometimes added. Two principal cases have to be considered:—(a) If the tabloid does not effervesce when dissolved in water the saccharine is present as saccharinate, (b) If effervescence results free saccharine is present and reacts like an acid on the bicarbonate. I. *No Effervescence.*—The alkalinity of the substance is first determined, so that the excess of NaHCO_3 can be estimated. For this purpose 100 mgrms. of the product are dissolved in cold water and titrated with $\text{N}/10 \text{ H}_2\text{SO}_4$. One cc. $\text{N}/10 \text{ H}_2\text{SO}_4 = 0.084 \text{ gm. NaHCO}_3$. To determine the saccharine the total sulphur is estimated. 100 mgrms. are mixed with 2 grms. of a mixture of equal weights of sodium nitrate and carbonate, and the mixture is fused. It is allowed to cool, taken up with hot water, acidified with HCl , and precipitated when boiling with BaCl_2 in slight excess. The precipitate is filtered off, ignited, and weighed. 233 parts of BaSO_4 correspond to 183 of saccharine and 233 of sodium saccharinate. II. *Effervescence.*—The alkalinity of the product is first determined and expressed in terms of NaHCO_3 as before. From another portion of the sample the free saccharine is extracted by anhydrous ether, the solution is filtered into a weighed vessel, the ether is evaporated off, and by weighing the amount of saccharine is ascertained. If the product consists of sodium bicarbonate and saccharine only the amount of NaHCO_3 saturated by the saccharine during solution is calculated, and then NaHCO_3 in excess + NaHCO_3 saturated + saccharine = practically 100. If the sum is less than 100 the saccharinate must be determined by ascertaining the amount of saccharine in the residue from the extraction with ether:— NaHCO_3 in excess + NaHCO_3 saturated + saccharine + sodium saccharinate = practically 100. If the sum is still less than 100 the lactose must be determined. The most common impurity is parasulphamide benzoic acid. It may be determined by hydrolysing with dilute hydrochloric acid, and allowing the liquid to crystallise after boiling for two hours with a reflux condenser. The crystals may be filtered off, washed, dried, and weighed, or the acid may be dissolved in alcoholic ether, from which it can be again separated by evaporating off the solvent.—*Annales des Falsifications*, 1918, No. 121, p. 369.

MEETINGS FOR THE WEEK.

- MONDAY, 24th.—Royal Society of Arts, 4.30. "Scientific Problems of Electric Wave Telegraphy," by Dr. J. A. Fleming.
- TUESDAY, 25th.—Royal Institution, 3. "The Dynamics of Flying," by Capt. G. P. Thomson, M.A.
- Royal Society of Arts, 4.30. "Key Industries," by E. J. Duveen.
- WEDNESDAY, 26th.—Royal Society of Arts, 4.30. "The Wage Problem in Industry," by W. L. Hichens.
- THURSDAY, 27th.—Royal Institution, 3. "How Silk is Grown and Made," by Prof. H. Maxwell Lefroy.
- Royal Society, 4.30. "Scattering of Light by Solid Substances," by Hon. R. J. Strutt. "Constitution of Sulphur Vapour," by Sir James Dobbie and I. J. Fox. "The Pressure upon the Poles of the Electric Arc," by W. G. Duffield, T. H. Burnham, and A. H. Davis.
- FRIDAY, 28th.—Royal Institution, 5.30. "Ether and Matter," by Sir Oliver Lodge, Kt.
- SATURDAY, March 1st.—Royal Institution, 3. "The Empire's Share in England's Wars—Eastern Empire," by The Hon. J. W. Fortescue.

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THE CHEMICAL NEWS

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THE CONCEPTION OF THE CHEMICAL ELEMENT AS ENLARGED BY THE STUDY OF RADIO-ACTIVE CHANGE.*

By FREDERICK SODDY.

(Continued from p. 87).

Period of Average Life.

THE law of radio-active change, which is the same for all cases, is that of unimolecular reaction, the rate of change, or quantity changing in unit of time, being a fraction, designated by λ and known as the radio-active constant, of the amount present. The value of λ , although vastly different for different radio-elements, is an absolute constant, so far as is known, for any one element, independent of every consideration whatever. The period of average life is the reciprocal of this constant, but the actual life of any one atom may assume any value. This is an experimental fact very difficult to account for. For example, it is quite easy to compare the value of λ for a collection of atoms (1) only just produced and not in existence a short interval before, and (2) that have remained undistinguished from an originally very much greater number, and each of which has been in existence many times the period of average life. In both cases the value of λ is the same. This fact excludes from consideration as a conceivable cause of disintegration any gradual progressive alteration in the atom during its period of existence, as, for example, was at one time suggested, a gradual radiation of internal energy by the electrons in their orbits within the atom. So far, we must admit, the cause of atomic disintegration remains unknown, although Lindemann (*Phil. Mag.* 1915, [vi.], xxx., 560) has attempted, with some success, to frame a theory to account for it.

Branch Series.

The development of the various radio-active sequences revealed that sometimes the series branches, and that in the change of one radio-element sometimes two products result, in general, in different amounts. Thus the uranium series at one point branches into the radium and actinium series, in proportion 92 to 8 out of 100 atoms disintegrating. Again, in the case of radium-C and thorium-C a similar branching occurs, and here in one branch an α -ray change is followed by a β -ray change, and in the other branch the sequence is reversed. These cases are sufficiently explained if it be supposed that two simple radio-active changes are in progress in the same substance simultaneously, and that each obeys the law of simple change as though the other did not occur. The distribution of the original substance into the two products is then proportional to the relative rates of the two changes. If λ_1 and λ_2 are the radio-active constants of the two changes, the proportion between the two products is as λ_1 to λ_2 , and the constant of the double change as a whole, $\lambda_1 + \lambda_2$. For thorium-C, the ratio is as 65 to 35, but for radium-C 99.97 to 0.03. The first is relatively easy, but the second extremely difficult to follow experimentally. It is, for example, impossible to follow further what occurs to the minor branch owing to the minuteness of the quantity of material, and although this has to be represented as not further changing, we have only negative evidence to go on. This branching is very important as showing how from one element two products or more in very different quantity may result, and may be the ex-

planation of the excessive rarity of certain of the elements in nature.

History of the Analysis of Matter.

The second, and in many respects even more revolutionary phase in the development of the study of radio-active change arose out of the chemical characterisation of the successive products, but some historical comment on the various influences which have gone to shape the current conception of the chemical element may be of interest before dealing with this development.

The analysis of matter into different chemical elements was at first concerned with known materials obtainable in abundance. The question, then, was not as to the existence or otherwise of certain elements, but whether certain thoroughly well-known substances were elements or compounds. Boyle's original celebrated definition was a purely practical one. That was to be regarded as elementary which could not by any means be separated into different substances. Almost at once, however, there crept into the interpretation of this conception two fallacies, or two aspects of the same fallacy, implicit in all the later characterisations of the elements, right up to the present time, namely, first that chemical analysis was necessarily the most fundamental and searching kind of material analysis, known or to be discovered, and, secondly, that chemical compounds were necessarily more difficult to resolve than simple mixtures. Any means soon came to mean any chemical means, and the element, in consequence, the chemical element. So was taken the first step which ultimately was to make the term *chemical element*, as it is at present understood, denote a definite but highly complex chemical conception, incapable of being defined or even understood without long years of training in the science, and totally different in every single respect from what a plain man or a beginner in the subject might reasonably suppose the term element ought to connote. The elementary and even the homogeneous character has departed from the conception of the chemical element, but the conception remains, and, whatever we choose to call it, will remain. The criterion of the chemical element soon came to be, in fact, the possession of a unique chemical character, distinguishing it and sufficing for its separation from all other elements. To this Dalton added a new criterion, the magnitude of the weight of the atom of the element, and each element unique in chemical character (as it happened) proved also to possess a unique atomic weight.

The discovery of the periodic law introduced the idea of families of chemically analogous elements, the members of which recurred after regular intervals when the elements were arranged in order of atomic weight. With the exception of hydrogen, every element became one of a group all totally distinct, but with obvious similarities. Boyle's practical definition of the element as that which could not be further resolved, more and more, as the century advanced, fell into desuetude. It became replaced by a theoretical conception, to which subsequently I propose to apply the term "heterotope," meaning the occupant of a separate place in the periodic table of elements. With this place came to be associated the unique chemical character, unique atomic weight, and later unique spectrum. On the claims of a substance to the title of element, as in settling disputes as to what multiple of the equivalent was to be adopted as the atomic weight, the periodic law became the court of appeal. Did a claimant to the title of element fit into a vacant place in the family of related elements? If it did, not only was there no doubt as to its atomic weight, but it certainly could scarcely be an ordinary compound or mixture. Whatever the elements were, it was clear that they were all of a class, the limits of chemical analysis, and, if complex, then all probably of the same kind of complexity.

Incidentally, also, the periodic law showed that although there was a connection between atomic weight and

* A Lecture delivered before the Chemical Society, December 19, 1918.

chemical character, there were exceptions, like tellurium and iodine, where the atomic weights appeared to have been reversed. This made it perfectly plain that it was merely a chance that no two elements happened to possess the same atomic weight. Dalton, as we shall come to describe, discovered in the atomic weight not merely a new atomic property, but a new class of atomic property which, until the present century, remained the only one of the kind known, and is concerned with a different region of the atom from that to which physical and chemical character, position in the periodic table, spectrum, and other identifying characteristics are to be referred.

The discovery of spectrum analysis led to the recognition of many new elements, cesium and rubidium, thallium, indium, helium, and gallium, all being so recognised before anything at all was known as to their other properties. In each case unique spectrum was later found to correspond with unique chemical character—except for the argon gases, all characterised by absence of chemical character—and unique atomic weight.

Again, the first fruits of the discovery of radio-activity were the recognition of the new elements polonium, radium, and actinium by their unique radio-active character in the first place. Then, in the case of radium, its claim to the title of element was confirmed, first by its exhibiting a unique spectrum, then by its possession of unique chemical character and atomic weight and by its occupying a vacant place in the periodic table. The emanations, next, as occupying a place in the family of argon gases, were easily characterised, and for the radium emanation unique spectrum was proved. Its origin from radium by loss of one α -particle gives the atomic weight as 222, which agrees with determinations of its density and rate of diffusion. The chemical characters of polonium and of actinium are different from those of the elements they most closely resemble. Polonium, or radium-F, by its close chemical analogy to both bismuth and tellurium, was characterised as an element of the sulphur family occupying the vacant place contiguous to bismuth. Actinium, by its resemblance in chemical character to the rare earths, and especially to lanthanum, although capable of being concentrated fractionally from that element, was reasonably supposed to occupy the vacant place in Group III, between radium and thorium. As will later appear evident, both these elements in due course may be expected to show unique spectra.

Further progress in the elucidation of the chemical character of successive products then underwent an abrupt and, at first, very puzzling change of direction. As member after member in the series was distinguished and characterised by its unique radio-active character, by its disintegration in definite and characteristic ways at definite and characteristic rates, no further chemically new elements were discovered. *Unique radio-active character does not always, as it did with radium, imply unique chemical and spectroscopic character.* The new members resembled known elements in chemical character so closely that they could not be separated from them by chemical analysis, although sharply differentiated from them by the radio-active properties. Radio-lead or radium-D cannot be separated from the lead which, being a product of uranium, accompanies it always in uranium minerals. Ionium, the direct parent of radium, cannot be separated from thorium; but the most instructive case, historically, which shows well how the new method of radio-active analysis serves to distinguish different elements, where chemical analysis fails, was the case of radiothorium.

Chemically Non separable Elements.

Ramsay and Hahn, in the course of working up a large quantity of thorianite for radium, observed in fractionating the radium from the barium in the usual way that the activity of the material concentrated at both ends of the fractionation. The activity accumulating in the more soluble fractions was due to a new product, which they termed radiothorium. It produces thorium-X, the thorium

emanation, &c., in successive changes. Naturally enough, they thought they had separated radiothorium by chemical processes from thorium, but they had not, for that, as we know, is quite impossible. Then Hahn found along with the other end fraction, containing the radium, a further new product, meso-thorium, which is intermediate between thorium and radiothorium. The radiothorium they had separated from thorianite was not that present in the mineral when they started, but that which had re-formed from the mesothorium after it had been separated from the thorium in the mineral. Could any more elegant extension, not merely of knowledge, but of the means of obtaining knowledge, be imagined? Two different elements, thorium and radiothorium, which on account of their chemical resemblance could not be individually recognised, and in the original interpretation of the thorium disintegration series were taken as one, became individually knowable, because the latter is the product of the former through the intermediary of a third member, mesothorium, possessing chemical properties totally unlike either. Radio-active change thus became the means of a new analysis of matter, for which there is no counterpart outside the radio-elements.

In turn, mesothorium suffered analysis into two successive products, mesothorium-1 and 2, the first distinguished by long period of life and a rayless disintegration into the second, which has a short life and gives powerful β - and γ -radiation in its change into radiothorium.

I then found that mesothorium-1 was chemically non-separable from radium, a discovery also made by Mackwald at the same time, and in 1911 I pointed out that in an α -ray change, such as ionium into radium, radium into emanation, thorium into mesothorium-1, and other cases, the expulsion of the α -particle causes the radio-element to shift its place in the periodic table by two places in the direction of diminishing mass and diminishing valency, whereas in successive changes in which a particles are not expelled, it frequently reverts to its former position, as, for example, radiothorium from mesothorium and lead from radio-lead.

To those actually engaged in the task of trying to separate the successive products of radio-active change by chemical analysis, it soon became clear that the chemical resemblances disclosed between certain of the members was such as to amount to chemical identity. The most obstinate cases of similarity previously known, among the rare earths, for example, cannot be compared with them. In all cases, radio-active methods afford the most delicate means for detecting the least alteration in the concentration of the constituents, and the most prolonged and careful attempts fail to produce a detectable separation.

At my request, Fleck undertook in my laboratory a systematic chemical examination of all the members of the series still imperfectly characterised, from the point of view of first finding which known element they most resembled and then finding whether or not they could be separated from that element. His researches were the means of finally unmasking the extreme simplicity and profound theoretical significance of the process of radio-active change. All the members of the series so far chemically uncharacterised he found to be chemically non-separable from one or other of the known elements, mesothorium-2 from actinium, radium-A from polonium, the three B-members and radium-D from lead, the three C-members and radium-E from bismuth, actinium-D and thorium-D from thallium.

Radio-active Change and the Periodic Law.

In February, 1913, K. Fajans in Germany, from electro-chemical evidence, and in this country A. S. Russell and I independently, from Fleck's work, pointed out the complete generalisation which connects chemical character and radio-active change. In addition to the shift of two places in the periodic table caused by the expulsion of the α -particle, it was now clear that the expulsion of the β -particle caused a shift of one place in the opposite

direction. Since the α -particle carries two atomic charges of positive electricity and the β -particle one atomic charge of negative electricity, the successive places in the periodic table must thus correspond with unit difference of charge in the atomic structure, a conclusion reached later for the whole periodic table, as far as aluminium, as the result of Moseley's investigations on the frequency of Barkla's characteristic X-radiations of the elements.

The non-separable elements, with identical chemical character, on this scheme were found all to occupy the same place in the periodic table, and on this account I named them isotopes. Conversely, the different elements recognised by chemical analysis should be termed "heterotopes," that is, substances occupying separate places in the periodic table, but themselves mixtures, actually proved or potential, of different isotopes, not necessarily homogeneous as regards atomic weight and radio-active character, but homogeneous as regards chemical and spectroscopic character, and also physical character, so far as that is not directly dependent on atomic mass.

Spectra of Isotopes.

As regards the spectrum, the first indication that chemically non-separable elements probably possessed identical spectra arose out of the failure of Russell and Rossi and of Exner and Haschek in 1912 to detect any lines other than those of thorium in the spectrum of ionium-thorium preparations that might reasonably be supposed to contain an appreciable, if not considerable, percentage of ionium. The work of Hönigschmid on the atomic weight of ionium-thorium preparations has fully confirmed this view. The isotopes of lead of different atomic weight separated from uranium and thorium minerals have been found to possess identical spectra. For this element, lead, Rutherford and Andrade have shown that the secondary γ -radiation excited by the impact of β -rays on a block of ordinary lead gave by crystal reflection two lines identical in wavelength with the two strongest lines in the γ -ray spectrum of radium-B, an isotope of lead, as Fleck showed, of atomic weight 214. This is of importance as indicating that X-rays and γ -rays, although no doubt originating in a deeper region of the atom than the ordinary light spectrum, do not originate in the deepest region of all to which the weight of an atom and its radio-active properties are to be referred.

(To be continued).

METHODS OF CALCULATING ADDED WATER IN MILK.

By LESLIE J. HARRIS.

In a previous communication dealing with the calculation of added water in milk (*Analyst*, 1918, xliii., 345) I proposed the use of the formula—

$$W = 100 - \frac{10,000 N}{8.5(100 - F) + 3N}$$

as being specially applicable to samples containing an excess of cream. By this formula the added water is calculated on the assumption that the original milk contained the *minima* of both fat and solids-not-fat, it being postulated that an accumulation of fat from F to F' is accompanied by a diminution of solids-not-fat from N to $N \times \frac{100 \times F'}{100 - F}$.

The formula above involves a rather long and unwieldy calculation. This may be obviated by having recourse to one of the methods below:—

1. *Calculation of Solids-not-fat in the Fat-free Milk.*—If the sample contains N per cent of solids-not-fat and F per cent of fat, the amount of solids-not-fat in the fat-free milk will be $\frac{N \times 100}{100 - F}$ and from this we may determine the extraneous water by reference to the table below.

For example, "milk" containing 10 per cent of fat and 3.88 per cent of solids-not-fat, contains in the fat-free portion $3.88 \times \frac{100}{90} = 4.31$ per cent of solids-not-fat, which is seen to be equivalent to a mixture of 50 parts of water with 50 parts of milk of the minimum standard.

In the table the values for *solids-not-fat in the fat-free milk* are calculated from—

$$\frac{(100 - \text{added water})}{100} \times 8.5 \times \frac{100}{100 - \frac{(100 - \text{added water})}{100} \times 3}$$

Mathematical reasoning will show that the results obtained from this expression are identical with those given by the formula.

Added water. Per cent.	Solids-not-fat in fat-free milk. Per cent.	Corresponding to solids-not-fat in milk of minimum standard. Per cent.
0	8.76	8.50
1	8.67	8.41
2	8.58	8.33
3	8.49	8.24
4	8.40	8.16
5	8.31	8.07
6	8.22	7.99
7	8.13	7.90
8	8.04	7.82
9	7.95	7.73
10	7.86	7.65
11	7.77	7.56
12	7.68	7.48
13	7.59	7.39
14	7.50	7.31
15	7.41	7.22
16	7.32	7.14
17	7.23	7.05
18	7.15	6.97
19	7.06	6.88
20	6.97	6.80
21	6.88	6.71
22	6.79	6.63
23	6.70	6.54
24	6.61	6.46
25	6.52	6.37
26	6.43	6.29
27	6.34	6.20
28	6.26	6.12
29	6.17	6.03
30	6.08	5.95
40	5.19	5.10
50	4.31	4.25
60	3.44	3.40
70	2.57	2.55
80	1.71	1.70
90	0.85	0.85

Rule.—To find the "solids-not-fat in fat-free milk," multiply the *solids-not-fat* by $\frac{100}{100 - \text{fat}}$; then find the corresponding figure for added water in Column I.

2. *Alignment Chart.*—Those who prefer a graphical method may make use of an alignment chart. The chart is read by means of a straight-edge, stretched thread, or line engraved on a celluloid cursor, &c. This line is made to coincide with the values for fat and solids-not-fat on the respective scales, and the percentage of added water is read off at the intersection with the third scale. A chart of moderate size will indicate the added water with an accuracy of about 0.5 per cent.

The chart is constructed on the principle of a nomogram ("Traité de Nomographie," Par Maurice d'Ocagne, Paris, 1899). The left-hand scale is divided logarithmically in an upward direction from 1 to 100, the figures for fat being complementary, and therefore at a distance from the base proportional to $\log(100 - F)$. The scale for

solids-not-fat is divided directly on the same logarithmic scale, but in a negative sense. The third scale is midway between the parallel to those for fat and solids-not-fat. If, now, the upper half of this scale be divided logarithmically from 1 to 100, a straight line joining the points representing 1 per cent fat and N per cent solids-not-fat will give a reading of $\frac{(100 - F)}{N}$ in the central scale. By

lowering the scale a distance $\log 8.5$, the readings will be multiplied by $8.5 \left(\text{i.e., } 8.5 \frac{(100 - F)}{N} \right)$, and by adding

3 units to each of the readings, converting these into their reciprocals, and multiplying by 10,000, the readings will

be of the value $8.5 \frac{(100 - F)}{N} + 3$. Since this is equivalent

to $\frac{10,000 N}{8.5 (100 - F) + 3 N}$, the scale readings will now give the percentage of milk (of the minimum standard) in the mixture, the complementary numbers given in the chart therefore representing the added water.

A further use of the chart is to determine the change in composition of any sample of milk under the action of gravity or centrifugal force; for example, given the fat and total solids in whole milk to find the amount of solids-not-fat which the skim milk would contain, and the composition of the cream for any concentration of fat. For this purpose all that is required is to place the straight edge coincident with the figure for fat and solids-not-fat, and rotate it around the point of intersection in the central scale until the new conditions are reached.

3. *Slide Rule.*—The principle of the alignment chart may be embodied in the form of a calculating rule. The reading for solids-not-fat on the lower scale is made to coincide with that for fat on the sliding scale; an arrow points to the percentage of added water on the upper scale. The rule is constructed in a precisely similar way to the alignment chart, except that the scale for added water is relatively twice as large, the percentages of added water being placed immediately opposite the figures for solids-not-fat in fat-free milk, as given in the table above. With the sliding scale in a given position, all possible corresponding combinations of fat with solids-not-fat are coincident.—*The Analyst*, February, 1919.

NOTES ON THE DETERMINATION OF PHOSPHORUS IN STEEL AND IRON.*

By W. D. RIDSDALE, F.C.S.

PART I.

THE principal object of this paper is to put before analytical chemists some details which the author has found to contribute to the exact and quick determination of phosphorus in steel and iron by the molybdate process, thereby making it at least equal in accuracy to the longer process in which silicon and arsenic are separated. After carefully looking into the conditions governing the precipitation of ammonium phospho-molybdate, a method was evolved which seemed to fulfil the necessary requirements, and after five years' regular use—in a standardised form—both under the author's own observation and also in numerous other works and independent laboratories in this country and abroad, during which time it was thoroughly tested against longer and more elaborate methods, it proved to be thoroughly reliable.

Comparison of Direct Molybdate Methods.

The first step taken was to compare the already published methods of this class and to make tests by as many as

possible. It was found that though the methods given by different authors were all similar in general procedure, on examining them in detail the conditions of precipitation differed widely as regards the amounts of acid and salts used. That such wide variations in these details and in the temperature and period of standing before filtering accounted for the co-precipitation of more or less arsenic and silicon, when present, was evident; consequently tests were next made under precise conditions, first of all on pure solutions of sodium phosphate and arsenate, and later on Standard steel samples, to determine the separate influence of acidity and various ammonium salts (chlorides, nitrates, and sulphates) on the tendency to precipitate the chief interfering element arsenic. The reason for trying the effect of ammonium chloride and sulphate was that they are often present as a result of adding either hydrochloric acid, a sulphate, or sulphite, to the solution for the purpose of reducing the excess of potassium permanganate usually added to oxidise the phosphorus and combined carbon.

Where either the free acidity was reduced, the ammonium nitrate increased, or ammonium chloride or sulphate added, in every instance the results were more or less high, even when the temperature of precipitation was as low as 40°. These experiments revealed several interesting features which should be observed in order to prevent arsenic from interfering with the precipitation of phosphorus (as ammonium phospho-molybdate) from pure solutions of sodium phosphate and sodium arsenate, viz.:—

(a) As much nitric acid (in proportion to the molybdc acid) should be used as permissible.

(b) The least amount of ammonium nitrate which is necessary should be used.

(c) No compound such as hydrochloric acid or ferrous sulphate which will result in chlorides or sulphates being in the solution should be introduced, as these salts favour the precipitation of arsenic even at as low a temperature as 40°.

(d) The precipitation temperature should not be above 60°. A few minutes' stand at this temperature before filtering gives a rather better separation from arsenic than sixty minutes at 40°.

Tests on standard steels in general bore out those obtained when working on synthetic solutions of sodium phosphate and arsenate, but showed that ferric nitrate (about 8.5 grms. per 100 cc.) appreciably retards the precipitation of arsenic and enables the precipitation temperature to be safely raised from 60° to 70°. In these particular circumstances ammonium sulphate instead of giving a high result appears to hinder the precipitation of phospho-molybdate.

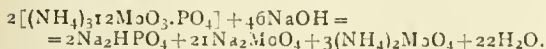
It cannot be emphasised too strongly that if a quick direct molybdate method is to be used yielding a high degree of accuracy equal to that of a long arsenic separated process, it must be carried out under carefully studied uniform conditions which can be readily reproduced.

The Author's Modified Process.

Method I.—Dissolve 2 grms. of steel in a covered conical beaker in 55 cc. nitric acid (sp. gr. 1.20 exactly). Remove brown fumes by gentle simmering, but do not heat strongly enough to evaporate any appreciable quantity of acid. Add 5 cc. potassium permanganate solution (50 grms. per litre). Boil gently for two minutes, when the phosphorus compounds should be completely oxidised to orthophosphoric acid. Add 10 to 13 cc. ammonium oxalate solution (40 grms. per litre), which should completely destroy the excess of permanganate and oxides of manganese in the liquid, and so cause it to turn clear. Simmer gently for two minutes longer. Add 15 cc. ammonium nitrate solution (600 grms. per litre). The volume should now be 85 cc. Bring to the boil, remove from heater, rotate liquid and pour into the centre of it 50 cc. cold (15–20°) neutral ammonium molybdate solution (50 grms. per litre). The temperature of precipitation will be within two or three degrees of 70°. Shake well for exactly two minutes;

* Abstract of a paper read before the Cleveland Institute of Engineers, February 10, 1919.

allow to stand at the temperature of the laboratory for not less than five or more than fifteen minutes. (If under 0.02 per cent phosphorus seems to be present it is advisable to allow to stand for the full fifteen minutes). The phospho-molybdate should now be completely precipitated free from silicon, arsenic, &c., and could be filtered and estimated by any of the usual methods. The author strongly recommends titration by means of standard $N/6.72$ (i.e., 100 cc. N diluted to 672 cc.) sodium hydroxide (free from carbonate) and nitric acid of the same equivalent strength. Then (number cc. of NaOH minus number of cc. of HNO_3) $\times 0.01$ = per cent phosphorus. The factor is the theoretical one based on the equation—



Under the conditions prescribed extensive tests have convinced the author that—contrary to the opinion at one time held by him—it is perfectly accurate to accept this calculated factor and is much to be preferred to standardising the solutions against a sample of "known" phosphorus content. A single estimation can be made in twenty to thirty minutes.

Method II.—For those preferring to use an acid molybdate solution the following modification can be made:—Dissolve the sample in 30 cc. instead of 55 cc. nitric acid (sp. gr. 1.20) and add 25 cc. of water (to keep the volume unchanged). Proceed as already described until the phosphorus is ready to be precipitated; then add a previously prepared mixture of 25 cc. ammonium molybdate (100 grms. per litre) poured into 25 cc. of nitric acid (sp. gr. 1.20); shake and finish as usual.

The method can readily be modified for the determination of phosphorus in hematite provided that the iron is practically free from titanium.

Method for Hematite Iron. III.—Dissolve 2.857 grms. of sample in 90 cc. nitric acid (sp. gr. 1.20) as for steel by gentle simmering.

Cool and dilute to exactly 100 cc. in a measuring flask. Filter through a dry multi-folded paper in a deep-ribbed funnel, and measure exactly 70 cc. (equals 2.0 grms. sample) of the filtrate into a 400 cc. conical beaker with a cover on. Heat to boiling point and proceed as described by the first method for steel, but use 60 cc. of cold ammonium molybdate solution instead of 50 cc. Finish as usual. A table was given showing a number of samples which were tested by the above methods. Samples ranging from very low (0.01 per cent) to very high (over 0.1 per cent) in both phosphorus and arsenic were purposely chosen so as to test the method under the most difficult set of conditions.

To those who are familiar with the "Analoid" system of analysis (see Note) it may be of interest to know that these are the investigations which resulted in the evolution of the "Ten Minute Pure (1914)" method, which—as pointed out in a paper recently given to the Society of Chemical Industry—has not been published before in any journal described to any society. ("Notes on Chemical Standards and their bearing on the Unification of Analysis," by C. H. Ridsdale and N. D. Ridsdale, given at Birmingham, November 27, 1918, and due to appear in the Society's *Journal*, February 15, 1918). In it, however, the method as here described differs in detail simply by the avoidance of solutions wherever possible and automatically bringing about precise conditions. This, together with the consequent concentration of liquid, permits the obtaining of equal accuracy in less time.

(Note.—This system was described by C. H. Ridsdale, F.I.C., F.C.S., and N. D. Ridsdale, F.C.S., in May, 1911, *Journal Iron and Steel Inst.*, 1911, 1, p. 332; No. 4 Session, 1911-12; *Proceedings of the Cleveland Institution of Engineers*, February, 1912; November, 1912, Part II., 1912, the Sheffield Society of Engineers and Metallurgists; March, 1913, Session 1912-13, *Proceedings of the Staffordshire Iron and Steel Institute*; May, 1918, *Journal Iron and Steel Inst.*, 1913, 1, p. 437; and by

W. H. Herdsman in November, 1911, Session 1911-12, *Proceedings of West of Scotland Iron and Steel Institute*).

PART II.

In order to meet the need for an alternative check method in which the arsenic is actually removed prior to the precipitation of the phosphorus, the following one can be confidently recommended. It is a modified form of a process published in "The Sampling and Analysis of Iron and Steel," by Bauer and Deiss (English translation), p. 240.

Determination of Phosphorus-arsenic Separated as Bromide.—Dissolve 3 grms. of steel or hematite iron in 25 cc. nitric acid (sp. gr. 1.42), followed by 15 cc. hydrochloric acid (sp. gr. 1.16), evaporate to dryness with a few fragments of clean silica brick to minimise spurting, and bake the residue ten minutes to complete the oxidation of the phosphorus and decompose nitrates. Take up with 40 cc. hydrochloric acid (sp. gr. 1.16) (owing to the excessive amount of graphite and silicon, hematite iron should be filtered at this stage and washed with hot water with a fine nozzle to keep the volume as low as possible). Add a gm. of zinc (granulated) and, when dissolved, add 5 grms. of ammonium bromide (crystallised) and carefully evaporate the solution to a paste as quickly as possible. This will eliminate all the arsenic chiefly as tri-bromide. Take up with 20 cc. hydrochloric acid, and in the case of steel samples, filter off silica, keeping the volume in the filtrate as low as possible. Oxidise the filtrate with about 10 cc. strong nitrate acid, added gradually, and evaporate if necessary down to about 70 cc. Cool, and add ammonia solution (sp. gr. 0.880) till a permanent precipitate of ferric hydrate is formed, then add 8 cc. of ammonia solution (sp. gr. 0.880), followed by 7 cc. nitric acid (sp. gr. 1.42). Boil and add nitric acid gradually until the precipitate is just completely redissolved. Evaporate if necessary to a volume of about 100 cc., then add a cold mixture of 20 cc. ammonium molybdate solution poured into 5 cc. of nitric acid (sp. gr. 1.42) and shake for two minutes. Allow the precipitate to settle for about five to fifteen minutes, filter, and estimate the phospho-molybdate by any of the usual methods.

A table was given showing a few of the results obtained by this method. In the first test ammonium bromide was intentionally omitted, and the result was 0.034 per cent high, thus proving that arsenic was not eliminated by a single evaporation with 40 cc. hydrochloric acid alone.

THE ORGANISATION OF CANADIAN CHEMISTS.

A PLEA FOR A DOMINION-WIDE NATIONAL SOCIETY.*

By Dr. FRANK T. SHUTT, Chairman, Ottawa Branch,
Canadian Section, Society of Chemical Industry.

GENTLEMEN,—My first words to you must be those of thanks and appreciation for the honour you have conferred upon me in electing me your chairman for the ensuing year. Many of you are, in person, unknown to me, but my sincere thanks are to you all—old friends and new friends alike. Of late years, and more particularly since the outbreak of war, the opportunities to meet my fellow chemists of the capital have been few. I am looking forward with pleasure to our meetings this winter, as offering excellent opportunities to "get together." I trust before our year is over we shall know one another better, both socially and professionally.

Although the Ottawa branch of the Society of Chemical Industry was organised towards the close of last season, we may fairly say that we are to night entering upon our corporate existence. Your Committee, and I am sure all of us, are very anxious that this first year in our history

* An address given before the Ottawa Branch, Society of Chemical Industry, December 5, 1918. From the *Canadian Chemical Journal*, January, 1919.

may be a very successful one, for a good beginning will go a long way towards putting this branch on a permanent basis. May I be permitted to emphasise one or two factors which I consider are essential to the success of our meetings?

The first is a good attendance. Nothing is more discouraging, nothing more effectually dampens enthusiasm than a poor attendance. Numerically, at the outset, we shall not be a strong body, and it will, therefore, be all the more necessary that every chemist in Ottawa should feel it incumbent to be present at the meetings. We shall also welcome all who may have an interest in the proceedings, and in this connection we might ask you to invite those of your friends interested in chemical matters.

Secondly, there is the matter of the programme. Your Committee has arranged a provisional programme for the season, which promises to be interesting and attractive. It may, however, be necessary to make one or two changes—the times are so uncertain and unsettled—and in that event, we shall look for volunteers among our members. There is no lack of excellent talent among the Ottawa chemists, and I know there is a large amount of valuable chemical work being carried on here. It will be the chief objects of our meetings to make this work known. Let us in this matter of programme learn to depend on ourselves. Let each one determine and plan to do his part in this matter, and we may have programmes fully equal in interest and value to those which our older sister branches in Toronto and Montreal have had for some years past.

May I add a further word to emphasise the importance of discussion—a well-ordered discussion—at the close of the papers. Discussion not merely adds life to a meeting, but is frequently the means of contributing additional data, additional information, fully as important as that presented in the paper. I shall look for the discussion to form an integral and important feature of the programme, and I trust that no diffidence will prevent you from doing your part in this matter.

The Organisation of Canadian Chemists.

Your Committee has selected as the subject for our consideration to-night the organisation of Canadian chemists. This is probably the most important matter of a general character that could engage our attention at this time. Many of us I know are of the opinion that the time has fully come in the history of Canada, when, alike in the interests of ourselves and of our country, there should be a closer linking up of the chemists at work throughout the Dominion. We all recognise the basic character of the relation that exists between the science of chemistry and our national manufactures and industries, and we are all firmly convinced of the vital importance of the application of chemistry to their development and welfare. The same is also true in respect to chemistry and our great national resources. Chemistry must play a very large and important part in their future economic development. Of agriculture, Canada's largest and most important industry, from an experience of more than thirty years, I can speak as one with some authority, and I can unhesitatingly say that all true and permanent progress will be, and must be, based on scientific work and investigation, and I will go further and say that of all the sciences taking part in this work—and they are many—chemistry is the one that above all others will, and must, take the first place. The problems in agriculture that await solution are practically innumerable and they are varied as to their character and nature, but I venture to say there are few of them that do not call at one stage or another in their working out for the assistance that chemistry only can give. There is a great future for profound, chemical, investigatory work in agriculture; would that those in authority had the knowledge and foresight to realise it.

But my point to-night is that whatever chemists and chemistry can do towards increasing the wealth and promoting the welfare and prosperity of the peoples of this Dominion, in the advancement of agriculture, in the

development of manufactures, in the working of our mines, our smelters and refineries, our wood and pulp industries, can be done more effectively, more economically if the chemists of this country have organisation. Whether this work be of the nature of the working out and control of processes, general analysis, or profound research, we feel confident that a closer organisation than now exists among Canadian chemists will conduce to greater progress and greater efficiency.

But before pursuing this subject further and indicating, as I hope to do in outline, the several advantages that may accrue from such an organisation, I wish from common gratitude to pay a tribute of thanks to that splendid British organisation to which we in Canada owe so much—the Society of Chemical Industry—and to place on record an expression of our high appreciation of all that it has done for chemists in Canada. It is the Society to which many of us here to-night are proud to belong, the society under whose auspices we meet this evening, nay more, we meet as a branch of its Canadian section and are, therefore, part and parcel of the parent organisation. It is this society that enables Canadian chemists to take the first steps towards organisation. This is something to be thankful for, something that we ought never to forget. As you are aware, as long ago as 1902, branches of this Society were formed in Canada—Toronto, Montreal, and Vancouver have had branches in successful operation for a number of years. In this, the Society has done a good work. It has helped us with prestige, it has helped us financially, and it has offered us an avenue for the publication of our work in the columns of its journal. For all this we would like to convey to our parent society our grateful acknowledgments.

It may be found after a thorough consideration of the whole matter that this relationship, which in a measure gives us a fellowship with the chemists of the Empire, is too valuable a one to cast off. A consensus of opinion and an inventory of our strength and resources may show that it is impossible for Canadian chemists to stand alone, and if such be the case, we must loyally and enthusiastically continue our work under the present auspices. No one will more heartily support the present arrangement than myself. It has worked satisfactorily in the past and it is quite possible it may meet our needs for the immediate future.

We have, however, to recognise that there has been a growing feeling of late among the chemists of this country that our affiliation with the Society of Chemical Industry does not offer the very best form of organisation for Canadian chemists. As evidence of this, I need only mention the recent formation of an independent association of chemists in Winnipeg, Manitoba—a mistake, in my opinion, but not one that is irremediable. However, at this juncture, I wish to very frankly state that I, to a very large degree, share in the opinion that the time has come to strike out for ourselves and form a Dominion-wide society—a Canadian Institute of Chemistry or a Canadian Chemical Society.

I wish, therefore, to place before you to-night for your consideration and discussion the desirability of one organisation of chemists for Canada, with a constitution that would enable it to enrol all *bonâ fide* chemists in good repute from the Atlantic to the Pacific. What, then, are the objects which we shall have in mind in considering this matter, what are the advantages to be gained by the establishment of a national society? These we will now briefly discuss.

First, there is the raising of the status of the Canadian chemist. This, to my mind, is the principal object we should have in our consideration of this subject. It may well be asked if the Canadian chemist, unless he holds a professorial position at a university, has any recognised professional status in this country. It is very doubtful if he has. Most certainly he does not rank with members of the medical and legal and engineering professions. Let me cite one or two instances in support of this statement.

A few years ago a well-known Canadian chemist, holding an important and responsible position in the country, was subpoenaed to give evidence in a case involving several millions of dollars. He prepared himself for the case, studying its various phases and aspects. He was on the stand for two days and his evidence covered many folios. He sent in an account for 200 dols., which he thought a modest sum under the circumstances. The Court ruled that he was entitled to 4 dols. a day and expenses, and that is all he received. That is an illustration of how the Courts of the land view or estimate the professional status of the Canadian chemist. Another instance, the Civil Service Commission is to-day advertising for a chemist who must be an honour graduate in chemistry of a recognised university, with at least one year's experience in analytical work of a certain specialised character, and the salary offered is 1300 dols. per annum. This is how our Government view the importance of the science of chemistry and the status of the profession. Do you think the Government would have advertised for a medical man or a lawyer or a qualified engineer at such a salary? I think not.

Well, if these instances are fair and representative—and I could cite many more, bearing on the same point—as, for instance, when a Minister of the Crown wanted me, not so many years ago, to accept as chief assistant in our laboratories at the Experimental Farm a clerk in a drug store, not discerning the difference between the nature of the work of a drug store and that of a chemical research laboratory—what, I ask, can we do to raise the status of the chemist? We certainly ought to do something. I do not see that there is any possibility of any advance in that direction until we have a national society, with high standards of membership—a society that, by its very constitution, its standing in the professional world, could in time create and exert an influence throughout the length and breadth of the land.

Then again, I think a national society of chemists of the nature I have indicated would be the very best protection the profession could have against the half-educated, poorly-equipped, and often not over-scrupulous chemist that is found practising, often for a reduced fee, in every country. We have them in Canada, and this country, as well as its responsible chemists, needs protection against them. Much money has been thrown away, as I very well know, on propositions floated on the strength of inaccurate and misleading analysis. Several instances of this nature, in connection with so-called potash discoveries in Western Canada, have come officially before me during the past two or three years.

Secondly, a national society would create a strength and an influence that could be used as occasion dictated in matters of moment to the country and its best interests. Of course, I refer only to matters of wide importance and which by their nature fall within the province of chemists to advise or offer an opinion upon. There ought to be, and I am sure there are, from time to time questions upon which a corporate body of chemists could, by public pronouncement and by memorials, well advise our people and their legislators. As, for instance, in establishing standards of quality for all classes of manufactured and industrial products, such as foods, fuels, &c., and in making of regulations which should safeguard the health of the workmen and the public generally. The industries look well after their own interests in such matters—that is true the world over—the public needs education and protection, and we as chemists have a responsibility in all this, which we ought not to neglect or ignore. There is in this a national work to be done, and it is only a national society that can do it.

Thirdly, a national society of high standing and with high ideals would act as a stimulus to more thorough, profound, and careful work by our Canadian chemists. It would furnish an incentive for the best work. Without a due realisation of the high character of our work, we become but drudges. Once chemistry is on a plane with

the so-called learned professions, the best of our men, the ablest, at our universities, would enter it; for chemistry not only ranks with the most interesting and fascinating of all sciences, but, as you will all admit, it offers problems and a field of research that call for the brightest intellects, the finest scholars the country can produce. Canada, as she grows, will need, and must have, more and more chemists, and chemists of the very highest ability. How else, I ask, is she to take a place in the front rank of civilised peoples?

Fourth, a national society would make possible a journal for the publication in Canada of Canadian work in pure and applied chemistry. This is something that we ought to have for our own use and information and in order to take our rightful place among the progressive nations of the world.

It is true we have a Canadian Chemical Journal (published in Toronto). We are very glad to have it; it is proving an interesting and useful publication from several points of view. But its sphere is necessarily limited, and it is not within its province to print papers on theoretical, abstract subjects and matters of pure research, of interest only to those who are engaged in, or interested in, the science of chemistry, apart from its application. The only avenue for the issue of such papers at present in Canada is in the transactions of the Royal Society of Canada, and this avenue does not seem to have appealed to very many of our chemists, possibly because of the restricted distribution of the transactions.

It is not necessary, I am sure, to enlarge upon the advantage of such a journal as I have spoken of. There ought to be a sufficiency of material to maintain a quarterly of high quality, and if at first there were a difficulty in getting papers of the right stamp, surely the very existence of such a journal would be an incentive, especially to our younger chemists, to enter upon investigatory work, for publication in its columns. It would be a matter of pride to us and all Canadians to have a journal of purely Canadian work. Presumably, at first, it would be a very modest affair.

As to the constitution of such a national society of Canadian chemists, I would to-night merely outline what might be desirable or possible. It is well that we should discuss this evening this phase of the subject, but, after learning the views of our members, those of the chemists throughout the Dominion must be ascertained, and the details should then be left in the hands of a strong and thoroughly representative committee.

Briefly, my idea would be a society that would include fellows, associates, and, if found practicable, general members. It might be modelled after the Institute of Chemistry of Great Britain and Ireland and the recently formed Australian Chemical Institute, though I am of the opinion that a Canadian society should be built upon a broader basis than either. It must be something more than a mere registration society, if it is to have a wide appeal and receive the necessary support for its maintenance.

The election of fellows and associates should be by examination or based upon chemical training, qualifications, and experience of the candidate. Each election should be approved by the central council of the society. A high standard should be insisted upon, so that the status of fellowship and associateship should be tantamount to, and generally and professionally recognised as equivalent to, chemical degrees.

I have said that, according to my views, the society should not be restricted in its function to registration, as, for instance, is the Institute of Chemistry of Great Britain. It should be a society that would bring its membership together for the reading of papers, for lectures and discussions on chemical matters generally, in as many branches as may be deemed necessary or desirable at centres throughout the Dominion. I am aware of the difficulties that would be met in establishing and maintaining a society which included the professional and non-

professional member. Whether these difficulties are insuperable I cannot say. If it were possible, I should like to see those interested in chemistry, but not professional chemists, find a place in the society.

The society would be governed by a council elected annually by the fellows and associates, and meeting, say, three or four times in the year for business at headquarters or at one or other of the large cities, as might be determined on. The society would necessarily have its charter fellows and associates elected, say, during the first year of its existence and drawn from the ranks of Canadian university professoriate, from the ranks of Government practising and industrial chemists, &c. The committee on constitution could make out a list of good men for consideration of the council. The fees, of course, would be graded, and each branch would have its own local officers. The society would undoubtedly require some financial assistance on the part of the Government, if it were to support a journal. If it could be shown that the society was really a good thing for Canada, such assistance should not be very difficult to obtain, and I think it could be demonstrated that a national society of chemists would prove a very valuable institution, not merely for the profession, but for the country at large.

In all this, I have not tried to exhaust the field. I have perhaps touched upon the more important and salient features in the matter of the establishment of a purely national society of Canadian chemists. It is not my desire in the least to impose my views upon you. In what I have said, I have endeavoured simply to place before you the main points, as I see them, that we must consider, and I trust that my remarks, necessarily of a fragmentary nature, may be of assistance in leading our discussion tonight into definite lines. Let our discussions have breadth. Let us, if possible, reach a decision on the main subject—the desirability of a Canadian Society of Chemists; we can well leave details for future consideration.

SCIENCE AND WAR.

RESEARCH WORK AT BIRMINGHAM UNIVERSITY.

In his report to the Council of the University of Birmingham, the Principal (Sir Oliver Lodge) states that the modern universities have amply justified their existence during the war. In them, as in the older universities, had been found the men of special knowledge and ability, and from them had emanated the instruments and devices which had enabled the country to deal with dangerous situations and solve problems of vital importance. Not at first were the universities fully utilised by military authority, but gradually their usefulness had become evident to many Government Departments, and, that being so, they would surely not much longer be allowed to suffer from the poverty which had retarded their development and curbed their enthusiasm.

Dealing with war services, from the scientific point of view, Sir Oliver states that in physics, research work had been unremittingly carried on. Dr. Shakespeare had been attached to the staff of a Royal Naval Experimental Station as consulting physicist. The work of Drs. Barlow and Keene had been privately printed by the Admiralty, and Mr. Daynes was engaged in the Research Laboratory of the War Office Aircraft Fabrics Department.

In chemistry nearly 4000 samples of coal tar and crude benzol had been examined for the Ministry of Munitions, and a number of confidential investigations, more especially for the Chemical Warfare Department and for the Department of Explosives Supply, had been carried on by Prof. Frankland, assisted by Dr. Challenger, Mr. Garner, and Mr. Wood. Prof. Frankland had been Deputy Inspector of High Explosives, and had been responsible for the testing and acceptance of the whole of the high explosives manufactured in the Birmingham area. He had also taken part in a special Government mission to Italy to

enquire into the resources of that country in respect of explosives and other war materials. He had also had much to do with the British anti-gas respirator, and had succeeded in getting the Italian Army equipped on the same plan. Dr. Frankland had also been chairman of the Chemical Section of the Royal Society War Committee and of the Reserved Occupations Committee. The D.S.O. had been awarded to Major McCombie, whose chemical knowledge had been effectively utilised at headquarters in France.

In mining, Sir John Cadman had been busily engaged in organising the new Petroleum Executive Department of the War Cabinet, of which he was director. He was also chairman of an Inter-Allied Petroleum Council, on which the United States, France, and Italy were represented, as well as the United Kingdom.

Prof. Lea, civil engineering, had served as a member of the Government Light Alloys Committee and the Oxygen Uses Committee, and the value of his work in connection with the design of Zeppelins and aircraft had been specially acknowledged. The professor of metallurgy, Dr. T. Turner, reported that researches for the Aeronautical Department were conducted in his laboratory by Mr. Belton and Mr. Wills, and that a department for copper and brass research had been opened in Birmingham under the Brass and Copper Tube Association, of which Prof. Turner was acting as honorary director. The Professor of Mechanical Engineering had conducted a number of experiments on tanks for the Trench Warfare Department.

Sir Oliver Lodge adds that the establishment of a special degree for training in research had been completed.

FEDERATION OF BRITISH INDUSTRIES.

THE Federation has had under consideration the means by which it could contribute to developing the commercial ties between Great Britain and the Dominions, and with this object in view has organised, with the support of the various Dominion representatives in London, a series of tours of members of the various Dominion Imperial Forces to the industrial centres of Great Britain.

The first of these tours started on February 18, when a representative party from the South African Imperial Force were entertained by the Federation at the Princes Restaurant, and left later in the day for Grantham. During their tour the South African representatives will have the opportunity of visiting the firms of Ruston and Hornsby, Ltd., the Birmingham Railway Carriage and Wagon Co., Ltd., the General Electric Co., Ltd., at Witton, the Wolseley Motor Co., Ltd., and the Handley Page Aeroplane Works.

It is hoped that as a result of these tours the South African representatives will obtain a useful insight into the productive power of the Mother Country, and will enter into personal relations with our leading manufacturers to the mutual benefit of South Africa and Great Britain.

The Federation considers that these tours besides being of commercial importance may serve as some small mark of the appreciation which is felt by British industry of the magnificent achievement of the Dominions during the war, and may in some small measure contribute to consolidate the ties of friendship which have grown out of the sufferings borne in common during the last four years.

TOUR OF BRAZILIAN DELEGATES IN GREAT BRITAIN.

With the object of strengthening the business and personal relations between Great Britain and Brazil, the Federation of British Industries has invited to this country a delegation of representative Brazilian business men. It may be recalled that this organisation was responsible for the visit of a body of Greek commercial men to the United Kingdom in the autumn of last year.

The reasons influencing the Federation of British Industries to select Brazil in the first instance from among the Latin-American republics may be very shortly stated. Brazil's area alone, covering more than half South America, entitles her to this preference apart from the moral influence exercised in that continent by her whole-hearted challenge to Germany at an early and critical stage of the war. The value of her co-operation was largely preventive so far as concerned the enemy's plans in South America generally. The services of Brazil's fleet patrols off the West Coast of Africa and at Gibraltar has also been amply acknowledged by our navy during the recent visit of the Brazilian Squadron to this country.

The time is therefore propitious for inaugurating a business tour, as the following notice of acceptance by the Brazilian Government shows:—

FOREIGN OFFICE AND BOARD OF TRADE,
January 30, 1919.

To the Director, Federation of British Industries.

SIR,—With reference to recent correspondence on the subject of the proposed mission of Brazilian business men to Great Britain, I have to inform you that a telegram has been received from His Majesty's Minister in Rio de Janeiro, to the effect that the latter has been informed by the Brazilian Minister for Foreign Affairs that the Brazilian Government is greatly pleased with the invitation which has been extended by the Federation of British Industries, and that careful attention will be given by the Ministry of Commerce to the names of the business men whom they would suggest should be invited.—Yours faithfully, (Signed) S. SPRINGER, for the Comptroller-General.

With a view to considering the representative industries of both countries which would best profit by the tour, it has been decided that Mr. W. S. Barclay, who was loaned by the Federation to Sir Maurice de Bunsen's Mission to South America during last summer, should proceed to Brazil and spend a few weeks there before conducting the delegates to this country. It has also been arranged, by courtesy of the Department of Overseas Trade, that Mr. Hambloch, H.M. Commercial Attache in Brazil, shall accompany the party to this country and throughout their tour, a fact which will be of very great advantage to the delegates.

Mr. Barclay will sail for Brazil on April 5, and will arrange for the tour to begin in this country not later than June 15.

THE SIR JOHN CASS TECHNICAL INSTITUTE.

THE annual distribution of prizes and certificates to the students of the above Institute took place on Tuesday, February 18, when the awards were distributed by Dr. CHARLES C. CARPENTER, Chairman of the South Metropolitan Gas Company. Sir THOMAS ELLIOTT, Bart., K.C.B., Chairman of the Governing Body, presided.

The Rev. J. F. MARR, M.A., Chairman of the Institute Committee, in the course of an account of the work of the past session, stated that 242 students and 17 members of the staff had served with H.M. Forces during the war, of whom 15 had given their lives in the service of their country.

In addressing the students, Dr. CARPENTER said that institutions such as the Sir John Cass Technical Institute appealed to him very strongly, primarily because they allowed the ordinary vocations of life to be carried on during the ordinary working hours, while the evenings were devoted to the extension of knowledge, so that practical experience and responsibility were associated with a full training in the principles of the sciences which formed the basis of industrial experience and progress. He remembered, as a young man, being confronted with problems at the works which he was unable to see through, but he also had a vivid recollection of the sudden rays of

light which were thrown upon that work after having had an opportunity, through a similar institution, of studying the science underlying the whole subject.

He went on to point out the importance of lucid expression, the putting down of results in clear and concise language. He also urged students not to ignore the great value of an elementary training in freehand drawing in order to be able to make, in the same way that one would make a note of a process or a reaction, a note of the apparatus concerned. Dr. Carpenter complained of the inertia of English manufacturers as compared with German manufacturers, in many instances it having been necessary to go to Germany when English manufacturers said certain requirements were impossible. That was one respect in which a great change must come over industry in Great Britain. The war had opened the eyes of manufacturers to the possibilities of what could be achieved by skilled and scientific management.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, February 13, 1919.

Sir J. J. THOMSON, President, in the Chair.

THE following papers were read:—

"Two Dimensional Solutions of Poisson's and Laplace's Equations." By L. BAIRSTOW, F.R.S., and A. BERRY.

Starting from a theorem stated in Lamb's hydrodynamics, problems involving solutions of Poisson's equation are interpreted in terms of the motion of the conventional inviscid fluid of hydrodynamics. The theorem states that the continuous acyclic motion of such a fluid inside or outside a rigid boundary can be reproduced by a system of sources round the boundary in all cases for which the fluid is at rest at infinity. The special point of the present paper is the formation and solution of an integral equation in order to find the strength of the sources. The answer appears as a series of integrals which is convergent in the four illustrations given; proof of convergence in the full mathematical sense is not attempted. The method of solution is applicable to boundaries of any shape and to more than one boundary. The integrals are easily obtained by graphical and mechanical methods.

The examples are—(1) The flow of an inviscid fluid round a cylinder; in this case the solution is exact. (2) The torsion of an elliptic cylinder, where again the solution may be completed analytically. (3) The torsion of a cylinder of which the section is that of an air-screw blade; the shape of section is such that analytical check is not possible. (4) The torsion of a hollow cylinder the section of which was made up of two eccentric circles; this was checked by comparison with the known analytical solution. In all cases the convergence of the series was satisfactory. Example (4) involves the solution of simultaneous integral equations; but the graphical processes are not intrinsically more difficult than for a single boundary.

"On the Cause of Hierarchical Order among the Correlation Coefficients of a Number of Variates taken in Pairs." By G. H. THOMSON, D.Sc.

From the tendency toward "hierarchical" order among correlation coefficients in mental tests, the conclusion has in the past been drawn that all these correlations are due to the presence of a general factor, and that none of them are due to group factors which run through two or more tests, but not through all. Although perfect hierarchical order can only be produced in this way, an approximation to perfection can be attained without any general factor, by leaving the number and identity of the group and

specific factors in each variate to chance. A card experiment is described in which this is done, and specimens of the resulting hierarchies are given. The proof depends on the formulæ of Pearson and Filon for the correlation of errors of correlation. If correlations are really all equal and positive, then these formulæ imply that sampling the population will give a set of observed correlations which are not arranged in haphazard order, but show hierarchical order. In the card experiment the hierarchical order is due not to sampling the population, but to sampling the elements of which the variates are formed. While the theory of a general factor is sufficient to explain the facts of psychological correlations, it is not necessary, for a wider theory, that mental tests or samples of some kind of mental elements do so also.

"The Transmission of Electric Waves round the Earth."
By G. N. WATSON, Sc.D.

From Austin's experimental results it appears that the magnetic force due to a Hertzian oscillator varies as $\text{cosec } \frac{1}{2} \theta \exp. (-A\lambda - \theta)$ at angular distance θ from the oscillator, where λ is the wave length and, in the case of signals over the sea, the constant A has the value 9.6.

It seems impossible to obtain any formula resembling this from a theory of pure diffraction, and it is therefore necessary to examine the hypothesis (put forward by Heaviside and others, and submitted to some analytical treatment by Eccles) that the upper regions of the atmosphere act as a reflector of the waves.

It is found that a formula of Austin's type is a consequence of this hypothesis, and that the numerical value of A given by Austin is obtained by assigning suitable values to the conductivity of the reflecting layer and its height above the surface of the earth. The problem of waves over dryland is also considered and the appropriate value of A is determined. A discrepancy between the formulæ obtained in this paper and Austin's formula should be noted, namely, that Austin's factor $\text{cosec } \frac{1}{2} \theta$ is replaced by $\sqrt{\text{cosec } \theta}$; but this alteration is of slight importance.

SOCIETY OF GLASS TECHNOLOGY.

Ordinary Meeting, February 19, 1919.

Mr. J. CONNOLLY in the Chair.

The first paper, entitled "*The Properties of the Lime Soda Glasses—(2) The Resistance to Water and other Reagents,*" by J. D. CAUWOOD, M.Sc., CONSTANCE MUIRHEAD, B.Sc., and W. E. S. TURNER, D.Sc., was read by the last named.

Several glasses have been melted on a small scale, and the lime content had been increased by definite amounts. The resistance of each glass to the following reagents:—Water, caustic soda solution, sodium carbonate solution, hydrochloric acid had been tested. In every case it was found that increasing the lime content brought about increasing resistance.

The second paper, "*The Properties of the Lime Soda Glasses—(3) The Thermal Expansions,*" by S. ENGLISH, M.Sc., and W. E. S. TURNER, D.Sc., was read by Dr. Turner.

The same series of glasses mentioned above (i.e., lime contents increasing to 10 per cent) had been tested in regard to thermal expansion. It had been proved that the expansion decreased as the lime content increased. Both papers proved the value of lime as a constituent of ordinary glasses.

Prof. P. H. BOSWELL, O.B.E., B.Sc., then addressed the Society on "*Impressions of the Glass Industry of the United States gathered on a Recent Visit.*"

First of all Prof. Boswell dealt with the supplies of raw materials as found in the States, and stated that six sands were in general use; one of them a beautiful sand from

Rockwood, Detroit, was used exclusively for optical glass. The American "sands" are not found as such, out in the form of sandstone (fairly soft). This is blasted, washed by water under pressure into the bottom of the pit, whence it is dredged up to the top of the pit. It is emptied into concrete bins, and worked down through steam pipes until it emerges as dry clean running sand. The top layer of steam pipes have a diameter of 3 in., the bottom 1 in., and there is about 1 in. clearance between the pipes. The sand is then loaded into covered wagons, each of which contains 50 to 80 tons of sand. The cost of labour in the sand pits is greater than that in this country, the workmen being paid about 1s. 6d. per hour, and yet the price of sand is less than that of English sand. The price of the washed dried sand at the pits varied from 5s. to 9s. per ton, and on the whole was superior to English sand. The cost of transportation also was less than in this country, the highest rate being about 5s. per ton. The fact that American sandstone firms can put their sand on the market so cheaply is due to the immense amount quarried per annum. One firm alone quarries nearly half a million tons per year. They calculated that the overhead charges for 200,000 tons are not much greater than for 50,000 tons. The quarrymen work about nine hours per day, but contract to keep the bins full, and thus work considerable overtime to make up for loss of output due to bad weather. Prof. Boswell afterwards dealt briefly with American supplies of potash and felspar, and then passed on to the question of refractories. He showed a specimen of a glasshouse pot, which had been developed by Dr. Bleininger, and this pot, after the melt had been performed, was perfectly white in colour and very close in texture. In making their pots the Americans were substituting Cornish kaolin by kaolin from Georgia, and were using ball clays from Tennessee and Kentucky in place of those from Devon and Cornwall. Considerable advances have been made in slip casting pots. One firm who were building pots in the English fashion used raw fireclay and grog. Tank blocks were also being made very successfully, and considerable research has been carried out on "humidity drying." There was also considerable manufacture of silica bricks in the States, the methods employed being much the same as in the United Kingdom, except that bricks were burnt for a much longer period than in this country. Dr. Boswell then dealt briefly with the various types of glass manufactured in the States, and laid special emphasis upon the number of labour-saving devices in use, which resulted in a huge output.

In the debate which followed, Capt. J. R. Clarke, Mr. C. J. Peddle, and Mr. F. G. Clarke took part.

Before the meeting the members of the Society paid a visit to the works of Messrs. Beatson, Clark, and Co., Ltd., at Botherham, and the thanks of the Society are due to the Directors for their kindness on the occasion.

The next meeting of the Society will be held at Birmingham on March 19, when a paper will be read the "Slip Casting of Pots."

Royal Institution.—Next Tuesday, March 4, at 8 o'clock, Prof. H. Maxwell Lefroy will deliver a lecture on "How Silk is Grown and Made—Mulberry Silk"; on March 11, "Insect Problems." On Thursday, March 6, Mr. Charles Aitken will give the first of two lectures on "Rossetti, Whistler, and Sargent." The Friday evening discourse on March 7, at 5.30, will be delivered by Prof. H. C. H. Carpenter on "The Hardening of Steel"; on March 14, Prof. A. Keith on "The Organ of Hearing from a New Point of View." On Saturday, March 8, at 3 o'clock, Prof. Sir J. J. Thomson, Professor of Natural Philosophy, Royal Institution, will give the first of a course of six lectures on "Spectrum Analysis and its Application to Atomic Structure." Prof. Hele-Shaw's lectures on "Clutches," announced for March 4 and 11, are unavoidably postponed until after Easter.

NOTICES OF BOOKS.

Organic Chemistry for Advanced Students. By JULIUS B. COHEN, Ph.D., B.Sc., F.R.S. Three Volumes. Second Edition. London: Edward Arnold. 1918. Pp. viii+366, vii+435, vii+378. Price 54s. net.

THE second edition of this work has been enlarged to such an extent that it has been found more convenient to issue it in three volumes instead of two; in its present form it gives a very comprehensive survey of the fundamental principles and recent developments of organic chemistry. The usefulness of the text-book has been thoroughly tested, and Prof. Cohen is to be congratulated upon having performed a remarkable achievement in its production. The first part deals with the reactions of organic chemistry, discussing their general nature and the methods and processes employed in bringing them about. The dynamics of organic reactions is also fully treated, and a new chapter has been added on abnormal reactions, in which steric hindrance and Victor Meyer's esterification law are both very fully treated. In the second volume the relation between physical properties and structure is discussed, and here a good deal of fresh matter has been inserted; isomerism, for example, being much more exhaustively treated than in the previous edition. In the third volume the synthetic methods employed in organic chemistry are described. Each volume is provided with both a subject and an author index, and is complete in itself.

BOOKS RECEIVED.

"Memorandum on the Industrial Situation after the War. The Garton Foundation." Revised and Enlarged Edition. January, 1919. Pp. 175. London: Harrison and Sons. Price 2s. net.

"Reconstruction Problems. 13. Rural Industries." London: H.M. Stationary Office. Price 2d. net.

CORRESPONDENCE.

DETERMINING THE COMPOSITION OF A MIXTURE OF SIMILAR SALTS OF TWO METALS.

To the Editor of the Chemical News.

SIR,—I was much interested in H. N. Wilson's description of a method for determining the composition of a mixture of similar salts without separating the mixture into its constituents (CHEM. NEWS, cxviii., 3). It is an

detailed account of this method (used to estimate the percentage of potassium iodide and sodium chloride in a mixture by converting them into the normal sulphates). For the last dozen years I have been under the impression that it was one of my original methods, but on looking the matter up I found this exercise grouped with two others, which makes it possible that the method was suggested by Dr. G. H. Bailey, then Senior Lecturer in Chemistry, although I do not think there is any reference to this method in his "Elements of Quantitative Chemistry," published in 1905. It is a type of experiment that "occurs" independently to different people. Some time ago I prepared a collection of exercises which might be worked out by this method with the intention of publishing them under the title of "Graphical Chemistry." The following were included:—

1. To find the Composition of Alloys.

(a) Containing two metals.

Weigh out a small portion of alloy. Dissolve in nitric acid. Evaporate carefully to dryness and heat until fumes cease to come off. Weigh. Suppose the alloy contains lead and zinc and one gram. of the alloy yields 1.153 grms. of the mixed oxides. The atomic weights of lead, zinc, and oxygen are 206.9, 65.4, and 16 respectively.

Then 1 gram. of an alloy containing 0 per cent of lead and 100 per cent of zinc yields 1.245 grms. of oxide, and 1 gram. of an alloy containing 0 per cent of zinc and 100 per cent of lead yields 1.077 grms. of oxide. The percentage composition of the alloy is found by finding the point of AB which corresponds to a weight of 1.153 grms. (See figure).

(b) If the alloy contains three (or more) metals.

i. Dissolve 1 gram. of alloy in nitric acid and convert the whole into mixed oxides, say 1.16 grms.

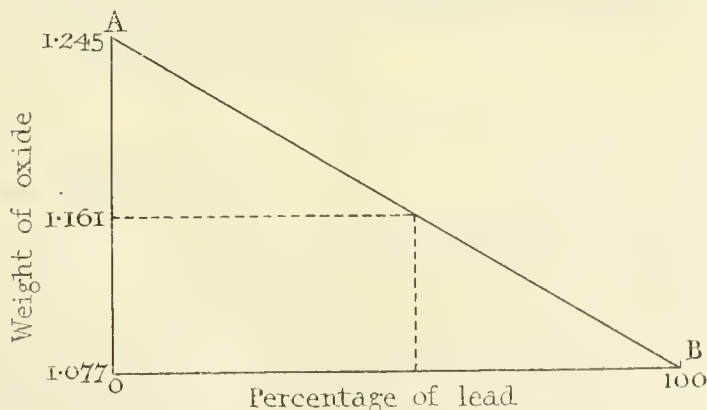
ii. Dissolve 1 gram. of alloy. Precipitate one metal, separate, redissolve, and if possible precipitate the metal again as hydroxide and convert it into the oxide. Suppose this metal be copper and yields 0.33 gram. of cupric oxide.

This corresponds roughly to $0.33 \times \frac{63}{79}$ grms. of copper.

Subtract this weight (0.26) of copper from the weight of alloy taken (1 gram.); also 0.33 gram. of cupric oxide from 1.16 grms. of mixed oxides. Then (1-0.26) grms. of an alloy containing A and B yields (1.16-0.33) grms. of their mixed oxides, and from the graph for these two metals the proportions of A and B can be determined.

I feel sure that any one who has many analyses of similar alloys to make would find this method a labour-saving device.

2. Assuming one standard solution to remain constant it is quite easy to check quickly all the others by graphical means.



old method, and at the end of a text-book that I used at Manchester University in 1904-1905 there is a

3. I prepared a number of "equilographs" to be used with my equalometer (see *School World*, May, 1917),

but the War made it impossible for my apparatus to be manufactured and has made the introduction of the equilographs less urgent. I prepared three of the latter by which one could read off from a graph the equivalent of any metal according to the amount of hydrogen liberated at N.T.P., or the amount of metallic oxide formed, or the weight of one metal displaced by another.

I believe that "Graphical Chemistry" has a future to the analytical chemist and will prove a great labour-saving device. As Mr. Wilson says, there is no limit to its application, and every hour saved contributes to greater output or greater leisure.—I am, &c.,

W. R. FIELDING.

Ierna, Galloway, Fleetwood.

MISCELLANEOUS.

University of Birmingham.—Prof. P. F. Frankland, Ph.D., LL.D., F.R.S., Dean of the Faculty of Science, University of Birmingham, has retired after long service at that University.

Appointment.—Dr. T. A. Henry, late Superintendent of the Laboratories at the Imperial Institute, London, has been appointed Director of the Wellcome Chemical Research Laboratories, London. Dr. F. L. Pyman, the former Director of these Laboratories, has accepted the Professorship of Technological Chemistry in the Manchester Municipal College of Technology, and in the University of Manchester.

MEETINGS FOR THE WEEK.

MONDAY, March 3rd.—Royal Institution, 5. (General Meeting).
TUESDAY, 4th.—Royal Institution, 3. "How Silk is Grown and Made—Mulberry Silk," by Prof. H. Maxwell Lefroy.
Royal Society of Arts, 4.30. "Science and Industry in Canada," by Prof. J. C. McLennan.
WEDNESDAY, 5th.—Royal Society of Arts, 4.30. "The Rubber Industry—Past and Present," by B. D. Porritt.
THURSDAY, 6th.—Royal Institution, 3. "Rossetti," by Charles Aitken.
Royal Society of Arts, 4.30. "The Need for a History of Bengal," by W. R. Gourlay.
FRIDAY, 7th.—Royal Institution, 5.30. "The Hardening of Steel," by Prof. H. C. H. Carpenter.
SATURDAY, 8th.—Royal Institution, 3. "Spectrum Analysis and its Application to Atomic Structure," by Prof. Sir J. J. Thomson, O.M.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—A. P. LAURIE, M.A., D.Sc.

SPECIAL FIRST, SECOND, and THIRD YEAR INTENSIVE COURSES for Students demobilised from the Forces will commence on APRIL 15 next and continue till JULY 25, in the subjects of—

MECHANICAL ENGINEERING,
ELECTRICAL ENGINEERING,
MINING ENGINEERING.

These Courses will be suitable for Students desiring to refresh their knowledge, or who wish to qualify for the Diploma of the College, and will count as equivalent to one year of the usual Three Years' Course for the Diploma, either in the First, Second, or Third Years.

Fee, £12 12s.; Matriculation Fee, 5s.

APPLIED CHEMISTRY.

Similar Courses in Applied Chemistry can also be obtained.

The attention of Demobilised Students is directed to the arrangements made by the Government for Payment of Fees and Maintenance of approved applicants.

Students desiring to enrol must apply, stating full particulars as to their pre-war University or Technical College training to the Interim Principal.

Analytical and Consulting Chemist, M.Sc.,
A.I.C. (Food and Drugs), will buy existing Practice or purchase Partnership with view to extension.—Address, Box 135, W. H. Smith and Son, Kingsway, London, W.C. 2.

Analytical Chemist with considerable experience, just released from Government work, wishes for a Position with an established firm, and would also consider Partnership with same or with Chemist who has had previous experience in Private Practice Work with view to opening out.—Address, "Analytical," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Assistant Works Manager seeks progressive
Position with Chemical Firm. Fully qualified Chemist. Twelve years' very varied Works experience. Good knowledge of Engineering. Accustomed to administration.—Address, A. W., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Analytical Chemist (Junior Assistant) for
Electrical Accumulator Works, London. Must be thoroughly used to Analyses of Lead, Lead Oxides, Acids, Waters, &c. Electrical knowledge an advantage. Salary to commence £200 per annum.—Write age, experience to Box 69, at Horncastle's, 60, Cheapside, E.C. 2.

Assistant Analyst (Woman), four years' experience in General Analytical Laboratory (Foods, Brewing-sugars and Malts, Chemicals, &c.), desires London permanency. Matriculated with Chemistry. Salary £150.—Address, V. A. H., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Demobilised Cadet (19) requires situation in
Laboratory. Good all-round education; Public School. Passed Inter. B.Sc. One year's previous experience.—Address, J. C. H., 23, Westcott Street, Hull.

Lady Chemist, Graduate, wanted for Chemical
Laboratory.—Apply, Chief Inspector, West Riding Rivers Board, Wakefield, stating present salary.

Trained Research Chemist, with Works experience, seeks Employment with Manufacturing Firm; or would make good Assistant to Private Investigator. London Degree; two languages; microscopy.—Address, T. R., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Works Analytical Chemist required. One
conversant with Soap Manufacture, Nicotine Extractions, and Agricultural and Horticultural Preparations. State full particulars and salary required.—Address, W. A., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Experienced Research Chemist and Analyst, with excellent Laboratory facilities in City, is now free to undertake RESEARCHES connected with the manufacture of CHEMICALS, INTERMEDIATES, DYES, &c.; also the Utilisation of WASTE PRODUCTS and all classes of ANALYSIS.—"Laboratory," 7, 8, & 9, Bolt Court, Fleet Street, London.

CORPORATION OF GLASGOW. GAS DEPARTMENT.

The Corporation invite applications for the position of **MANAGER** for their **CHEMICAL WORKS**. Applicants must be fully qualified Chemists, able to deal fully with all Liquid Products from Gas Works, to advise as to the introduction of all necessary up-to-date plant for the working-up of the By-products, and be competent to supervise the erection thereof.

Applications, stating salary required, age, qualifications, training, and experience, to be endorsed on the outside "Gas Department—Chemist" and lodged with the subscriber not later than **WEDNESDAY, 5th proximo.**

J. LINDSAY, Town Clerk,
City Chambers, Glasgow, Feb. 12, 1919.

LINEN INDUSTRY RESEARCH ASSOCIATION.

Applications are invited for the Post of **DIRECTOR OF RESEARCH** for the Linen Industry Research Association.

Candidates should state their Scientific and other qualifications, such as administrative, industrial, &c., and furnish the names of three references.

The functions of the selected candidate will be to make a survey of the entire field of Research in the Linen Industry from the growing of the flax to the completion of the finished product, to draw up a programme of Research, to organise the scheme, and to supervise its carrying out.

A salary of not less than £1000 a year is offered.

Further particulars and the Prospectus of the Association may be obtained from the **SECRETARY**, 3, Bedford Street, Belfast.

THE CHEMICAL NEWS

VOL. CXVIII., No. 3073.

THE CONCEPTION OF THE CHEMICAL ELEMENT AS ENLARGED BY THE STUDY OF RADIO ACTIVE CHANGE.*

By FREDERICK SODDY.

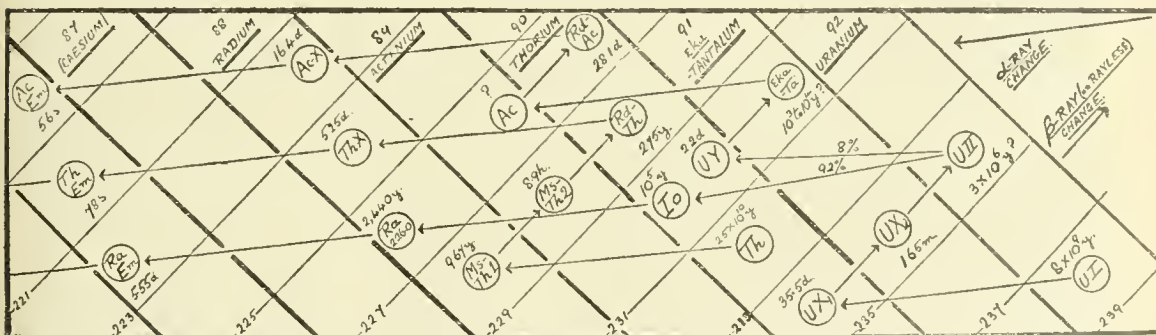
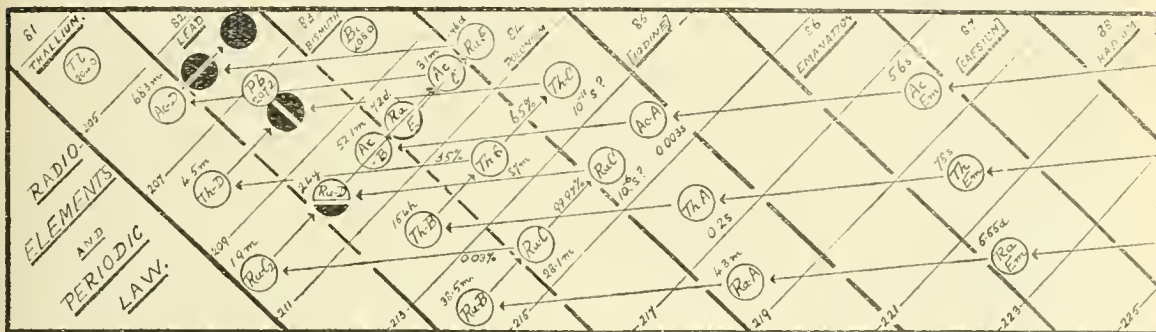
(Concluded from p. 99).

Description of the Figure.

THE generalisation, brought up to date, is set forth in the accompanying figure, which is to be read at an angle of 45°, making the lines of atomic weight horizontal and the division between the successive places in the periodic table vertical. Starting from uranium and thorium, the series run in an alternating course across the table and

intended to express any physical significance; but for the fact that many members would be super imposed, they would all be represented in the centre of the places. The periods of average life, which are always 1.443 times the periods of half-change, are shown for each member above or below its symbol, a ? indicating that the period is estimated indirectly from the Geiger-Nuttall relation.

The figures at the head of each place represent the atomic numbers or number of the place in the periodic table, starting with hydrogen as unity, helium as 2, lithium as 3, and so on. Moseley found that the square-root of the frequency of the characteristic X-radiation of an element was, for the K-series of radiations, proportional to integers less by one than the atomic numbers. Strictly speaking, there is no means of determining the absolute value of the atomic number, but the starting point having been fixed for any one element, the others can then be found in terms of it. Moseley assumed the atomic number of aluminium as 13, as it is the thirteenth known element in the list starting with hydrogen as unity. It is unlikely that any new elements will be discovered between hydrogen and aluminium, although if they were it would be necessary to alter the whole of the subsequent atomic



extend over the last twelve places as far as the element thallium. At this point, it is interesting to note that the expulsion of an α - instead of a β -particle would have resulted in the production of an isotope of gold, and so literally have realised the goal of the alchemist. As it happens, a β -particle is expelled and lead results, so far as the changes have yet been traced, in all cases as the final product.

It has been necessary, in order to separate the series from one another, to displace the actinium series to the right and the radium series to the left of the centre of the places, but this displacement within the single place is not

numbers to correspond. (The position of the stellar elements of Prof. Nicholson it is unnecessary to consider here, as the Chemical Society is shortly to be given a first-hand account of this fascinating question). For X-radiations of the other series, the square-roots of the frequencies are not proportional to integers even, although the differences are nearly integral for successive elements in the periodic table. The actual numbers in the figure, 92 for uranium, for example, are derived from the assumption that the atomic number of aluminium is 13, but it is well to remember that, although relatively to one another based on experimental evidence, the absolute value is to some extent arbitrary.

(We are indebted to the Chemical Society for permission to use this woodcut).

* A Lecture delivered before the Chemical Society, December 19, 1915.

The Chemical Character of the Radio-elements.

The simple connection between the sequence of radio-active changes and the chemical character of the products has effected an enormous simplification, not only in the theory, but also in the practice of radio-chemistry. The series extends over twelve places, two, namely, those in the families of the halogens and the alkali metals, being entirely skipped. In the ten occupied places are forty-three distinct types of matter, but only ten chemical elements. Seven of these ten, thallium, lead, bismuth, emanation, radium, thorium, and uranium, can now in every respect be considered, both chemically and spectroscopically, thoroughly well known. These seven places accommodate all but nine of the known radio-elements, and these nine, the isotopes of polonium, actinium, and ekatantalum, respectively, are the only members the chemistry and physics of which cannot be referred to well-known elements obtainable in sufficient quantity for ordinary chemical and spectroscopic examination.

Of these three, polonium, although the element of which at present the chemistry is best known, is likely to remain the most difficult to bring into line with the others, for, although a vast amount of exact information has been obtained as to its reactions, it would seem to remain hopeless ever to obtain it in anything but infinitesimal amount owing to its relatively very short period.

The chemistry of actinium has been enormously simplified by the discovery that mesothorium 2 is isotopic with it, for the latter may be used as an indicator to show in what way the actinium distributes itself after any chemical treatment. Owing to its relatively small quantity as a branch product and to the fact that, itself, it gives no rays, the characteristic radio-activity of its products only making their appearance slowly after it has been separated, actinium has always been a difficult element to extract from the mineral and very easy to lose in chemical operations. There is now, however, another reason which will assist in the study of this element.

The Origin of Actinium. Ekatanalium.

The generalisation has now led to the elucidation of its origin and the discovery of its direct parent. From its constant association with uranium minerals, and the relative activity therein of its products in comparison with the activity of those of radium, it was considered to be a branch product of the uranium series, only 8 per cent of the atoms of uranium disintegrating passing through the actinium series and 92 per cent through the radium series. Its definite location in the periodic table, by virtue of its isotopy with mesothorium 2, made it clear that its parent must either be in the radium, or the ekatantalum place, the former if it is produced in a β -ray change and the latter if it is produced in an α -ray change.

The ekatantalum place was vacant when the generalisation was first made, but it was necessary to suppose that uranium-X, like mesothorium, comprised two successive products, uranium-X₁ and uranium-X₂, both giving β -rays, and the latter occupying the vacant place in question. This prediction was confirmed within a few weeks of its being made by the discovery by Fajans and Gohring of uranium X₂, or brevium, a new member responsible for the more penetrating β radiation given by uranium X, and having a period of only 1.65 minutes. The possibility that actinium was produced in a β -ray change from an isotope of radium was experimentally disproved, and there remained only the second alternative, which was rendered the more probable by the existence of a member, uranium-Y, discovered by Antonoff, isotopic with uranium X₁, and simultaneously produced with it from uranium in relative quantity such as is to be expected, if it were the first member of the actinium series. Uranium-Y, like uranium-X₁, gives soft β rays, and hence its unknown product must be the isotope of uranium-X₂, and might also well prove to be the unknown direct parent of actinium in an α -ray change of long period.

During the year the missing element has been found in two independent investigations (Soddy and Cranston, *Proc. Roy. Soc.*, 1918, [A], xciv., 384; O. Hahn and L. Meitner, *Physikal. Zeitsch.*, 1918, xix., 208). The problem as it presented itself to us was so to treat a uranium mineral as to separate an element, if present, which possessed the chemical character of the known but hopelessly short lived uranium-X₂, using the latter as an indicator in trying possible methods beforehand. The method adopted, distillation at an incipient red heat in a current of carbon tetrachloride vapour and air, was found to be very effective in volatilising uranium-X₂ from uranium X₁, and when applied to pitchblende it was found to give a product in which none of the known pre-emanation members of the disintegration series were present. Thus was obtained a preparation from which actinium was at first absent, but which, with the lapse of time, continuously generated actinium, as characterised beyond the possibility of doubt by means of its active deposit.

It should be mentioned that the exact point at which the uranium series branches has not yet been definitely ascertained, as there is a choice of alternatives, at present experimentally indistinguishable. Uranium-Y may be either the product of uranium I or of uranium-II, and the latter alternative, which is that shown in the figure, is taken for the present as likely to be on the whole the more probable. The point can only be settled by the determination of the atomic weight of ekatantalum or actinium.

Independently, Hahn and Meitner obtained the parent of actinium from the insoluble siliceous residues left after the treatment of pitchblende with nitric acid by adding tantalum, and then separating it and purifying it by chemical treatment. They showed that it gave α -rays of range 3.14 cm. of air at N.T.P., and, from this range, estimate its period to be from 10^3 to $2 \cdot 10^4$ years. There should therefore be sufficient of the element in uranium minerals to enable the spectrum, atomic weight, and chemical character of the pure substance to be determined in the same way as for radium. Its separation on a large scale will enable actinium itself to be grown in a pure state, analogously to the preparation of radiothorium from mesothorium, and so should allow the spectrum at least of actinium to be found.

With regard to the period of actinium, there is at present a real conflict of evidence, and so it is impossible to say whether our knowledge of actinium is ever likely to become as complete as that of radium, or to remain, like that of polonium, confined to what can be learned from infinitesimal quantities. Cranston and I, on certain assumptions, concluded from indirect evidence that the period of actinium was 5000 years, but Hahn and Meitner, on the other hand, state that they have obtained evidence confirming Marie Curie's provisional estimate of the period as about thirty years, from the direct observation of the decay of the radiations of a sealed actinium preparation.

Atomic Weight of Isotopes.

It is clear that the periodic law connects, not primarily chemical character and atomic weight, but chemical character and atomic charge or atomic number, which alters its value by integers, not continuously, producing the step-by-step changes in chemical character which is at the basis of the analysis of matter into the chemical elements, or heterotopes. This atomic number is, however, the algebraic sum of positive and negative charges, so that the loss of the α particle with its two positive charges and of two negative electrons as β -particles leaves its value unchanged and produces an isotope of the element having an atomic weight four units less than the original. Unique chemical character and unique spectrum reaction is no proof of homogeneity, and so we arrive at the conclusion that the chemical elements, so far considered homogeneous, may be mixtures of isotopes, possessing different atomic structure and stability, revealed when they undergo radio-active change, and in some cases

also different atomic weight. This, although within the scope of the Daltonian analysis of matter to detect, nevertheless, until radio-active investigations revealed this possibility, remained overlooked. In two cases, that of the isotopes of lead on the one hand, and of ionium and thorium on the other, this difference of atomic weight in elements spectroscopically and chemically identical has now been established by direct determination.

The figure shows that, so far as these changes have been followed, they all terminate in the place occupied by lead, and, if this is the real, as distinguished from the apparent end in all cases, all the ultimate products are isotopes of lead with atomic weight between 210 and 206. The product of radium-C₂, in the branch claiming only 0.03 per cent of the whole ultimate product of radium, with atomic weight 210, may be left out of account as being negligible, and also the product of the actinium branch for which the atomic weight is still uncertain; but the main products, namely, that of uranium with atomic weight 206, and both the thorium products in the two branches, with atomic weight 208, are different in different directions from that of common lead with atomic weight 207.2.

The conclusion that the ultimate product of thorium, as well as of uranium, was lead, was quite new and opposed to the opinion of those who had made a special study of the Pb/U and Pb/Th ratios of radio-active minerals of various geological periods. I found, however, that the atomic weight of the lead separated from Ceylon thorite was 207.7, and Hönigschmid confirmed this with a specimen of my material and obtained the figure 207.77. Just recently, from a specimen of lead separated from a Norwegian thorite by Fajans and his co-workers, he has found the value 207.90 (*Zeitsch. Elektrochem.*, 1918, xxv., 163). Whereas the same investigator, and also T. W. Richards and others, have found values for the atomic weight of lead separated from uranium minerals all lower than that of common lead, and in two cases from carefully selected minerals between 206.0 and 206.1. I found my thorite lead was denser than common lead in the same proportion as its atomic weight was greater, and the densities of the various specimens of uranium lead have been found by Richards to be less than that of common lead, the atomic volume for all varieties being constant. The spectra of these various isotopes have been repeatedly examined, but hitherto no differences whatever have been established. Haskins and Aronberg (*Proc. Nat. Acad. Sci.*, 1917, iii., 710), for ordinary lead and uranium-lead of atomic weight 206.34, examining the strongest line, 4058, in the sixth order of spectrum obtained by a 10 inch grating, observed a constant difference of 0.0043 Å., but are themselves disposed to await further further results before drawing any conclusions.

The atomic weight of a mixture of ionium and thorium was found by Hönigschmid to be 231.51 as compared with 232.12 for thorium, the spectra being identical and impurities absent in both specimens. The calculated value for the atomic weight of ionium is 230, and the evidence, so far as it yet goes, is in accord with the view that, in the mixture examined, about 30 per cent was ionium and 70 per cent thorium. By a simple comparison of the emanating power of the mixture with that of the pure thorium preparation under similar conditions, the proportion of ionium to thorium could be readily determined directly, since ionium does not give an emanation, and this unknown eliminated, but this has still to be done.

The Different Varieties of Isotopes and Heterotopes.

When isotopes, such as those just considered, possess different atomic weights, it is to be expected, although this has not yet been practically accomplished, that a separation by physical means, such as prolonged fractional diffusion, ought to be possible. Chlorine and other elements, the atomic weights of which depart largely from an integral value, seem to deserve a further physical

analysis by this method. Sir J. J. Thomson's positive-ray method of gas analysis ought to be able to detect such isotopes of different atomic weight without separation, and at one time it seemed that neon had been so resolved, but this has not yet been confirmed. Mr. Ashton tells me this work is still being actively prosecuted at the Cavendish Laboratory.

It would be interesting also if the rotation of the salts of some optically active acid with different varieties of lead, separated from uranium and from thorium minerals, were examined. A difference is to be expected, although it is likely to be small, and possibly may be too minute to be detectable. Recent experiments at Harvard have shown that the refractive index of a crystal of lead nitrate is independent of the atomic weight of the contained lead, but the solubility, as is to be expected, is different, the molar solubility of different varieties being the same.

Isotopes need not, however, have different atomic weights. One of the clearest cases is in the two end-products of thorium, but, if the scheme is correct as regards the branching point of the actinium series, ionium and uranium-Y, actinium-A and radium-C', actinium C and radium-E, actinium-B and radium-D, and the actinium and uranium isotopes of lead, are other cases. These result by branchings of the series, and, since in the respective branches the amount of energy evolved in the successive changes is different, the internal energy of the various pairs must be different, although for them atomic weight as well as spectroscopic and chemical character are all identical. I recently suggested in the case of the two end-products of thorium that possibly only one of these survives in geological time, namely, that produced in the smaller quantity, and that the other continues to break up in changes as yet undetected (Royal Institution Lecture, May 18, 1917; *Nature*, 1917, xcix., 414 and 433). This would account for the relative poverty of thorium minerals in lead, which was the original basis for the conclusion that lead was not the ultimate product of thorium. The point still remains experimentally untested. Isobaric isotopes of the character in question can only at present be distinguished if they are unstable and break up further, but they must be taken into account in any theoretical conception we form of the ultimate structure of matter. The accomplishment of artificial transmutation would reveal them if they existed, and the discovery of any new property, like radio-activity, concerned with the nucleus of the atom rather than its external shell, might also be the means of revealing differences of this character.

On the other hand, the production of isobaric heterotopes is the ordinary consequence of β -ray changes, single or successive. Such heterotopes, possessing different chemical and spectroscopic character but the same atomic weight, have been recently termed *isobares* by A. W. Stewart (*Phil. Mag.*, 1918, [vi.], xxxvi., 326), who, following Fieck's work on the chemical resemblance, not amounting to non-separability, between quadrivalent uranium and thorium, has drawn a parallel between them and elements existing in more than one state of valency, as, for example, ferrous and ferric iron.

The extent to which the study of radio-active change has enlarged the conception of the chemical element may be summarised by the statement that now we have to take into account in our analysis of matter, not only the heterobaric heterotopes before recognised, but also heterobaric and isobaric isotopes and isobaric heterotopes or isobares.

The Nuclear Atom.

I have attempted to present the most important facts of radio-active change without introducing any theory or hypothesis at all as to the structure of the atom. I think it important to keep the two matters distinct. Our knowledge of electricity, which in its modern phase may be considered to start from the relatively recent discovery of the electron, is still far too imperfect to enable any com-

plete theory of atomic structure to be formulated. My task would be incomplete, however, if I did not refer briefly to the nuclear atom of Sir Ernest Rutherford, which may be regarded as the logical descendant of the earlier electronic atom of Sir J. J. Thomson. The weakness of the latter was that it took account essentially only of the negative electrons, and its attempt to ascribe the whole mass of the atom to these nearly massless particles involved the supposition that a single atom may contain hundreds of thousands of electrons. The actual number is now known to be rather less, as an average, than half the numerical value of the atomic weight. Although unsatisfactory in accounting for the mass of the atom on an electronic basis, it was much more in line with present views in accounting for chemical character and the arrangement of elements in the periodic table. The root idea that the successive elements in the table are distinguished by the increment of one electron in the outermost electronic ring, followed, as period succeeds period, by the completion of this ring and the formation of a new external one, so that members of the same chemical family have similar external ring systems, is still the most probable view yet advanced. In conjunction with the conception of the nucleus and the gradual unravelling of the various series of characteristic X radiations, both experimentally and by mathematical analysis, it bids fair soon to give a definite concrete picture of the structure of all the different elements (compare L. Vegard, *Phil. Mag.*, 1918, [vi.], xxxv., 293).

As regards the deepest region of atomic structure, wherein radio-active phenomena originate, the nuclear atom is the only one proposed that has any direct experimental foundation. It is based on the deflections suffered by the α -particle in its passage through the atoms of matter, on the one hand, as Bragg showed many years ago, on the exceedingly slight deviation of the overwhelming majority of the α -particles, and, on the other hand, on the subsequently discovered large deviations suffered by a minute proportion. The nuclear atom is a miniature solar system, like most model atoms, the negative electrons occupying the atomic volume by their orbits around a relatively excessively minute central sun or nucleus, wherein the atomic mass is concentrated, and consisting of an integral number of atomic positive charges equal to the atomic number of the element, and the number of electrons in the outer shell. An α -particle is the nucleus of the helium atom, and, unless it passes very near the nucleus of the atom through which it penetrates, its path is practically undeflected. The few that chance to pass close to the exceedingly small but massive central nucleus are swung out of their path like a comet at perihelion, save that the forces at work are regarded as repulsive rather than attractive.

It appears from radio-active change that atomic disintegration occurs always in the central nucleus, both α - and β -particles originating therein. The atomic number of the element is its net nuclear charge, the difference between the positive and negative charges entering into its constitution. Of all properties, mass and radio-activity alone depend on the nucleus; the physical and chemical character and the spectrum of an element originate in the outer shell. The character of the outer shell is fixed by the net charge, not at all by the mass or internal constitution of the nucleus, and the integral variation of this charge from 1 to 92 gives the successive places of the periodic table. Expulsion of two β - and one α -particle in any order gives an isotope of the original element with atomic weight four units less. Isobaric isotopes resulting in branch changes differ only in the internal structure and stability of the nucleus. The atomic mass is the only nuclear property known before the discovery of radio-activity, and, except as regard this, the whole of physics and chemistry up to the close of the nineteenth century had not penetrated beyond the outer electronic shell of the atom. Even now, mass and radio-activity remain the sole nuclear properties known.

Conclusion.

Nemesis, swift and complete, has indeed overtaken the most conservative conception in the most conservative of sciences. The first phase robbed the chemical element of its time honoured title to be considered the ultimate unchanging constituent of matter; but since its changes were spontaneous and beyond the power of science to imitate or influence to the slightest degree, the original conception of Boyle, the practical definition of the element as the limit to which the analysis of matter had been pushed, was left essentially almost unchanged.

The century that began with Dalton and ended with the discoveries of Becquerel and the Curies took the existing practical conception of the chemical element and theorised it almost out of recognition. The element was first atomised, and then the atom was made the central conception of the theory of the ultimate constitution of matter, on which modern chemistry has been reared, and from which its marvellous achievements, both practical and theoretical, have mainly sprung. The atom and the element became synonyms, related as the singular to the plural, and implicit throughout this century was the assumption that all the atoms of any one element are identical with one another in every respect. The only exception is in Sir William Crookes's conception of "meta-elements" as applied to the rare earths. Here the idea was rather that of a gradual and continuous difference among the different atoms of the same element, the properties of the latter being the mean of those of its individual atoms. Modern developments have tended definitely away from rather than towards this view.

The second phase in the development of radio-active change has now negated each and every one of the conceptions of last century that associated the chemical element with the atom. The atoms of the same chemical element are only chemically alike. Unique chemical and spectroscopic character is the criterion, not of a single kind of atom, but rather of a single type of external atomic shell. Different chemical elements may have the same atomic mass, the same chemical element may have different atomic masses, and, most upsetting of all, the atoms of the same element may be of the same mass and yet be an unresolvable mixture of fundamentally distinct things. Present-day identity may conceal differences for the future of paramount importance when transmutation is practically realised. Then it may be found that the same element, homogeneous in every other respect, may change in definite proportion into two elements as different as lead and gold. The goal that inspires the search for the homogeneous constituents of matter is now known to be, like infinity, approachable rather than attainable. The word homogeneity can in future only be applied, qualified by reference to the experimental methods available for testing it.

All this, of course, does not in the least affect or minimise the practical importance of the conception of the chemical elements as understood before these discoveries. Every chemist knows the conception has had and will continue to have a real significance as representing the limit of the spectroscopic and chemical analysis of matter which remains, although it is now known to convey something very different from the original and natural conception of the chemical elements as the *l m n's* of the material alphabet.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 3rd inst., Sir James Crichton-Browne, J.P., F.R.S., Treasurer and Vice-President, in the chair. The Hon. R. S. Cripps, Major G. Dennison, Major C. de Roemer, Miss M. R. Dreschfield, W. H. Eccles, F. H. A. Engleheart, L. F. A. Fogarty, Dr. W. A. Frost, A. A. Hall, Dr. S. F. Harner, A. Meade, G. Newgass, E. Y. Radley, E. K. Rideal, Dr. R. E. Slade, W. Symington, Miss E. G. Western, G. Williams, and Miss M. Xavier were elected members.

THE DETERMINATION OF PHOSPHORUS IN VANADIUM STEELS, FERRO-VANADIUM, NON-VANADIUM STEELS, AND PIG IRON.

By CHAS. MORRIS JOHNSON.

1.—Method for Steel containing Vanadium up to 2.6 per cent.

IBBOTSON and Brearley, in 1902 ("Analysis of Steel Works Materials"), recommended that phosphorus be precipitated from the reduced solution of vanadium, using ferrous sulphate as a reducing agent, claiming thereby to aid in the precipitation of phosphorus when vanadium is present.

Cain and Tucker, in 1913, recommended that the vanadium present be reduced with ferrous sulphate and sulphurous acid for the same purpose (*Journ. Ind. Eng. Chem.*, 1913, v., 647).

The method here described gives a successful and convenient method for complete precipitation of phosphorus in the presence of highly oxidised vanadium.

Place 1.63 grm. sample in 150 cc. beaker. Dissolve in 45 cc. HNO_3 (1.13 sp. gr.) over a low flame. When solution is clear and brown fumes have been driven off, add 3 cc. KMnO_4 solution; boil three minutes, then add 3 cc. FeSO_4 solution to dissolve precipitate due to the excess permanganate; boil until brown fumes are gone. Avoid large excess of ferrous sulphate.

Add 40 to 50 cc. concentrated HNO_3 (1.42 sp. gr.), bring to a boil, rinse cover and sides of beaker with least amount of distilled water, then add 50 cc. of the water solution of ammonium molybdate. Stir vigorously for a minute or two, and let stand over night.

Decant through a 7 cm. paper, placing a little paper pulp in apex of filter, keeping the main precipitate in the beaker. Wash iron out of filter by washing 15 times with the nitric wash, then proceed to pour the main precipitate on to filter.

Transfer all of precipitate as far as possible, with the aid of the nitric wash. Add about 2 cc. of wash to the beaker and remove adhering particles with a rubber-tipped glass rod. Use separate beaker for catching washings. Wash 15 times with the dilute nitric wash, then 25 times with KNO_3 wash, or until the outside of the filter has no sour taste, especially along the double thickness.

Place filter containing washed precipitate in 150 cc. beaker, add enough standard NaOH solution to cause the yellow colour of the precipitate to disappear on macerating the paper to a pulp with a rubber-tipped stirring rod. Dilute to about 30 cc. with distilled water, add a drop of phenolphthalein solution, which should cause a deep red coloration, otherwise more standard NaOH solution is needed; then titrate back carefully with standard HNO_3 solution until the pink just disappears. Subtract total cc. of acid used from total cc. of alkali used. The difference in cc. $\times 0.01$ = percentage P.

TABLE I.—Showing Effect of Increasing amounts of Nitric Acid (1.42 sp. gr.) on Phosphorus Recovery.

(This work was done with 1.63 grm. samples of U.S. Bureau of Standards, 0.120 P standard, 10b).

Vanadium	15 cc. HNO_3 added.	30 cc. HNO_3 added.	40 cc. HNO_3 added.	50 cc. HNO_3 added.
Per cent.	P found.	P found.	P found.	P found.
None	0.121	0.121	0.121	—
0.20	0.119	0.121	0.121	—
0.40	0.114	0.118	0.121	—
0.60	0.111	0.117	0.120	—
0.80	0.110	0.116	0.121	—
1.00	0.110	0.115	0.120	0.119
1.40	0.110	0.112	0.121	0.122
1.80	0.105	0.112	0.119	0.121
2.20	0.099	0.111	0.119	0.120
2.60	0.093	0.108	0.117	0.117

Remarks.—The tests with the higher vanadium content were more tardy in precipitating than the lower ones, though all settled well after forty minutes standing. Those to which 15 cc. conc. HNO_3 were added gave deep orange precipitates, darkening in colour about in proportion to the vanadium content, clinging tightly to the stirring rods and beakers. The three highest vanadiums are lower in yield of phosphorus than the preceding ones because of the impossibility of detaching the adhering precipitate from the stirring rods.

Those with 30 cc. conc. HNO_3 were an improvement in speed of precipitation, colour of precipitate, and cleaning from beakers and rods. Those with 40 cc. and 50 cc. showed the best coloured precipitates; i.e., nearest the normal yellow phosphomolybdate colour, and gave water-white washings, from which no recoveries of phosphorus were made. The 50 cc. ones were a little prompter than the 40 cc., though both sets were a vast improvement over the 15 cc. and 30 cc., and both cleaned very easily from beakers and rods and gave good results.

The precipitate from the 15 cc. conc. HNO_3 in particular seemed to be too finely divided, and passed through the pores of the filter, necessitating reprecipitation of the washings in all those of higher vanadium content.

The vanadium was added as nitrate from an acid solution made as follows:—Fuse 4.5 grms. V_2O_5 (56.14 per cent V) with 10 grms. Na_2CO_3 in a platinum crucible for ten to fifteen minutes. Let cool, place in a 400 cc. beaker, add 10 cc. water, then HNO_3 (1.20 sp. gr.) until effervescence ceases, and 25 cc. in excess. Rinse off crucible thoroughly with distilled water, cool solution to room temperature, transfer to 500 cc. flask, dilute to the mark with water, stopper, and shake to mix thoroughly. One cc. = 0.00505 grm. V. One per cent V in 1.63 grm. sample = 3.25 cc. solution.

The vanadium was added after the tests were weighed and before the 45 cc. HNO_3 (1.13 sp. gr.) were added. The vanadium was, in each instance, reduced from yellow to green, due to the action of the reducing gases liberated by the reaction between the acid and the steel. The 40 to 50 cc. conc. nitric added just before removing from the fire caused the yellow vanadic colour to return.

Solutions Required.

Nitric Acid for Titrating.—Dilute 35.4 cc. HNO_3 (1.42 sp. gr.) to 4000 cc. with distilled water.

Stock Solution of Sodium Hydroxide.—Dissolve 150 grms. NaOH (C P. sticks) and 1 grm. Ba(OH)_2 in 1000 cc. water. Stir well, and allow to stand twenty-four hours. Filter off the clear solution (or decant if preferable), and dilute with an equal volume of distilled water. Put into a 2-litre bottle, and close with a rubber stopper.

Sodium Hydroxide Solution for Titrating.—Dilute 566 cc. stock solution to 8000 cc. with distilled water.

Ferrous Sulphate Solution.—Dissolve 55 grms. steel (low in phosphorus and sulphur) in 1000 cc. beaker in 720 cc. H_2SO_4 (1:3). Add a little water occasionally to prevent salting out, and heat gently, but do not boil. Filter, cool, and dilute to 1000 cc.

Concentrated Potassium Permanganate Solution.—Dissolve 50 grms. KMnO_4 in 1000 cc.

Nitric Wash.—Dissolve 8 grms. KNO_3 in 8000 cc. water.

Acid Wash.—Dilute 102.4 cc. HNO_3 (1.42 sp. gr.) to 8000 cc. water.

Faintly Ammoniacal Water Solution of Ammonium Molybdate.—Into each of four 800 cc. beakers weigh 55 grms. ammonium molybdate and 50 grms. ammonium nitrate, and add 40 cc. ammonium hydroxide (0.95 sp. gr.). Dilute each to 700 cc. with water. Heat for about thirty minutes, stirring once in a while until all salts are in solution. Combine contents of the four beakers by pouring into a large bottle, then dilute to 4000 cc. with water. Let stand over night. Filter the insoluble material through double 15 cm. papers. Do not wash. The clear

solution thus obtained should remain clear indefinitely. Do not filter out the insoluble material until the total mixture from the four beakers has stood over night.

II.—Method for Phosphorus in U.S. Standard Steels and Pig Irons to which have been Added 28 per cent Vanadium and in Ferro vanadium containing 56.7 per cent Vanadium.

Procedure.—Weigh out 0.5 grm. steel and 0.5 grm. V_2O_5 (56.14 per cent V). Transfer to 250 cc. porcelain dish. Digest with a mixture of 30 cc. HCl (1.20 sp. gr.) and 30 cc. HNO_3 (1.42 sp. gr.) for about one hour, then rinse off cover, add 100 cc. HNO_3 (1.42 sp. gr.), and take to dryness. Bake five minutes at $750^\circ C$. in an electric muffle furnace.

Dissolve the oxides in 35 cc. conc. HCl, evaporate to 10 cc., add 50 cc. HNO_3 (1.42 sp. gr.), take to 10 cc. volume, then add 10 cc. more strong nitric acid, and heat awhile with cover glass on. Filter through a platinum Gooch crucible with a thin pad of acid-washed asbestos, using suction. Wash 15 times, using the following wash:—200 cc. HNO_3 (1.42 sp. gr.), 100 cc. water, and 20 grms. $Fe(NO_3)_3$. Ferric nitrate made by dissolving 5 grms. low phosphorus, melting bar steel in 50 cc. HCl (1:1) and taking to syrupiness twice with 50 cc. HNO_3 (1.42 sp. gr.) each time.

Concentrate the filtrate from the separated V_2O_5 to 10 cc. in 150 cc. beaker, and filter out the second crop of vanadium "rust" as before. A third concentration to 10 cc. should show no "rust" (V_2O_5).

To the third concentration add 40 cc. HNO_3 (1.42 sp. gr.), and bring to a boil, rinse cover and sides with water, and precipitate with 50 cc. of the faintly ammoniacal ammonium molybdate solution. Stir vigorously for about two minutes. Let stand one hour, filter, and wash as described for steels containing up to 2.6 per cent V. Titrate with alkali and acid in the usual manner.

TABLE II.—Results obtained Using this Method on U.S. Standards.

No.	Standard	V_2O_5 added. Mgms.	P found. Per cent.	Per cent P given by U.S. Govt
1.	Iron D, 6a V_2O_5 ..	500	0.522	0.526
2.	Iron D, 6b V_2O_5 ..	500	0.531	0.531
3.	10b V_2O_5 ..	500	0.124	0.120
4.	10b V_2O_5 ..	600	0.115	0.120
5.	No. 20 Std. V_2O_5 ..	500	0.033	0.031
6.	No. 20 Std. V_2O_5 ..	600	0.033	0.031

In the above procedure an average of 0.007 per cent was found in the V_2O_5 added.

TABLE III.—Phosphorus in Ferro-vanadium, 56.7 per cent Vanadium.

Author's method by removal of about two-thirds of V_2O_5 and precipitation with faintly ammoniacal ammonium molybdate solution (per cent P) ..	0.414 0.418 0.397 0.401
V_2O_5 reduced with Fe_2SO_4 and H_2SO_4 . Precipitation with acid molybdate solution. No V removed (per cent P) ..	0.240 0.232 0.235 0.228 0.234 0.260 0.220
Acid molybdate precipitation. No extra HNO_3 added. No V removed (per cent P) ..	0.053 0.108
Faintly ammoniacal ammonium molybdate precipitation plus 40 cc. HNO_3 (1.42 sp. gr.). No V removed (per cent P) ..	0.185 0.183

III.—Method for Determining Phosphorus in Non-vanadium Steels and Pig Iron, using a Faintly Ammoniacal Water Solution of Ammonium Molybdate.

Procedure.—Weigh 1.63 grm. sample into 150 cc. beaker. Dissolve in 45 cc. HNO_3 (1.13 sp. gr.) over low flame. (In case of pig iron and certain chrome steels, when all metal is in solution filter off carbon residue through 7 cm. paper, wash 15 times with dilute HNO_3 , wash, catching filtrate in 150 cc. beaker. Concentrate filtrate to original volume).

Add about 3 cc. of the $KMnO_4$ solution, boiling for three minutes, then just enough $FeSO_4$ solution (about 3 cc.) to dissolve the oxides of manganese. Boil off brown fumes. Add 15 cc. HNO_3 (1.42 sp. gr.). Rinse cover and sides of beaker with least amount of water, add 50 cc. ammonium molybdate solution, and stir briskly until phosphorus precipitate is completely formed (about two minutes stirring). Let stand half an hour or less. Filter through 7 cm. paper, wash 15 times with dilute HNO_3 wash, then with nitrate wash until the outside fold of the filter has no sour taste. In case of high phosphorus samples this may mean as much as 35 or 40 times.

(The washings in such a case were kept separate from the main filtrate, concentrated to 10 cc., acidified with 15 cc. conc. HNO_3 , and 50 cc. of the ammonium molybdate solution added. It was then allowed to stand over night. There were no recoveries, showing the insolubility of the precipitate in the wash).

TABLE IV.—Comparing Results obtained when using Faintly Ammoniacal Water Solution with those obtained by use of a Nitric Acid Solution of Ammonium Molybdate. (See Iron Age, April 5, 1917).

Sample No.	Slightly ammoniacal water solution of molybdate.	Nitric acid solution of ammonium molybda e.
	Per cent P found.	Per cent P found.
9 ..	0.054	0.056
34 ..	0.023	0.023
7132 ..	0.019	0.018
3622 ..	0.056	0.054
1 ..	0.013	0.014
2 ..	0.058	0.058
4 ..	0.042	0.044
5 ..	0.052	0.052
70,055 ..	0.055	0.052
80,042 ..	0.042	0.044
x, pig ..	0.736	0.730
r, steel ..	0.006	0.004
3641 ..	0.050	0.049
34 ..	0.025	0.025
39 ..	0.058	0.056
Pig iron Std. A ..	0.097	0.096

TABLE V.—Showing Results of Tests on U.S. Govt. Standards.

Sample.	P found.	U.S. Bureau P. value.
	Per cent.	Per cent.
Pig iron, D, third set ..	0.610	0.602
Pig iron, B 6a ..	0.104	0.105
Pig iron, D 6a ..	0.540	0.545
Steel, 10b ..	0.119	0.120

This method is the same as the one published by the author in *Iron Age*, April 5, 1917, except that it was afterwards found that more rapid precipitation of the yellow precipitate was secured by the addition of 15 cc. of concentrated nitric acid (or 30 cc. 1:1 acid is safer to handle) to the boiling solution of the sample just before removing from the fire to add the molybdate solution, and 1.13 sp. gr. HNO_3 is used instead of 1.20 as the steels in general dissolve more rapidly in the 1.13 acid.

Advantages of the Foregoing Methods for Ordinary Routine Work on Plain and other Steels.

1. The simplicity of the preparation of the faintly ammoniacal water solution of ammonium molybdate as compared with the elaborate method of preparing the old acid molybdate solution in nitric acid.

2. The handling of the acid molybdate is disagreeable, hard on the clothing and fingers of the operator and on table tops. The slightly ammoniacal water solution is harmless in these particulars.

3. As stated, the slightly ammoniacal water solution keeps as clear as distilled water after it has been properly filtered, and its precipitating power is constant, whereas the old acid solution soon becomes turbid, and therefore its precipitating power is continuously lessened.

4. The interference of vanadium up to at least 2.6 per cent V in the determination of phosphorus is prevented in a simple way, and the true phosphorus is obtained from ferro-vanadium containing the very high vanadium content of 56.7 per cent.

Acknowledgment.

Credit is due to Mr. F. D. Hawkins for his careful analytical work when making the trial analyses required by the author to prove the foregoing.—*Journal of Industrial and Engineering Chemistry*, xi., No. 2.

ZIRCONIA: ITS UTILISATION AS A REFRACTORY SUBSTANCE, AN OPACIFIER, AND AN ABRASIVE.*

By M. A. GRANGER.

ALTHOUGH zirconium is one of the relatively rare elements which have been known for a long time—it was discovered by Klaproth in 1789—for more than a century it has been of interest only to laboratory chemists. Deposits of zirconiferous minerals in spite of their number and variety were not extensive enough to warrant commercial exploitation. It is only recently that zirconia, in consequence of its remarkable refractory properties, has attracted the attention of metallurgists and those who have to employ really high temperatures.

The mineral which has been longest known as a source of zirconium is zircon, or zirconium silicate. Zircon occurs in more or less clear crystals possessing a bright sparkle. It is sometimes colourless, but usually has a more or less pronounced yellowish tint, according to the state of oxidation of the iron which accompanies it. The composition of the mineral, in accordance with the formula $ZrSiO_4$, would be silica 33.04, zirconia 66.96. Zircon occurs in various forms known as hyacinth, malacon, tachyphalite, oerstedite, auerbachite, crystalite, alvite. It is found in different localities—Ceylon, where it occurs in the form of sand, Russia (Urals), Austria (Tyrol), United States (North Carolina), Norway (near Brevik), France (Epailly, Mont-Dore).

Zircon from Ceylon and Epailly belongs to the variety known as hyacinth; it is red in colour and transparent. It is fairly hard, its hardness being 7.5. Its specific gravity varies from 4.05 to 4.70. It is not attacked by ordinary acids, but when reduced to a fine powder it is attacked by hot sulphuric acid. It is decomposed also when fused with bisulphates or alkaline carbonates.

A certain number of other zirconiferous minerals is known, but their chemical nature is more complex than that of zircon.

Rosenbuschite.—Monoclinic; fluo-silicate and titanate of zirconium, sodium, and calcium of formula $6CaOSiO_3 \cdot 2Na_2ZrO_2 \cdot F_2(Ti_2SiO_3 \cdot TiO_3)$.

Laavénite.—Monoclinic; fluo-silico-zirconate of sodium and calcium, containing iron, manganese, fluorine, and niobic acid.

Woehlerite.—Monoclinic; fluo-silico-zircono-niobate of calcium $2R.(SiZr)_2O_3RNb_2O_6$.

Hiortdahlite is a triclinic mineral to which the formula $4Ca(SiZr)_2O_3Na_2ZrO_2F_2$ is ascribed.

Eudyalite is rhombohedral; it is a metasilicate of the type $R'_4R''_2Zr(SiO_3)_7$, which may contain niobium or tantalum.

Catapleite differs from the above minerals in being hydrated; it corresponds to $H_4(Na_2Ca)ZrSi_3O_{11}$ and is hexagonal.

All these minerals are more or less vitreous or resinous in appearance, are less hard than zircon and lighter. Their coloration is variable, but mostly their tint is yellow or brown.

To give some idea of their complexity and the proportion of zirconium in them we have prepared the accompanying table, giving the analysis of some zirconiferous minerals.

The materials which we have just enumerated are the classical sources of zirconia, especially zircon. It is this last mineral which is mostly employed for the preparation of compounds of zirconium. The methods of treatment are tedious.

(i.) The powdered zircon is treated with potash in a silver crucible. It is taken up with water, treated with hydrochloric acid, and in the solution separated from silica the oxides of iron and zirconium are precipitated and taken up with oxalic acid which dissolves the iron oxide.

(ii.) Another method depends on transforming the zircon into zirconium chloride. Mixed with carbon and treated with a current of chlorine it gives volatile silicon chloride and zirconium chloride which condenses in the cold parts of the apparatus.

(iii.) Marignac removed accidental traces of iron by means of hydrochloric acid and acted on the powdered mineral with potassium hydrogen fluoride. Thus a soluble fluozirconate of potassium was obtained, and could easily be separated from insoluble fluosilicate. The zirconia could readily be extracted from it by first converting this salt into sulphate.

Such are the methods which were used in laboratories for the preparation of zirconia up to the time when the problem arose of preparing it in large quantities.

For some years it has been known that there is an important deposit of zirconia in Brazil at Porcos de Caldas, 200 kilometres from Sao Paul, in the State of the same name. According to E. H. Rodd (*Journ. Soc. Chem. Ind.*, 1918, xxxvi., 213) the deposit covers an extensive mountainous plateau, 48 km. long and 24 km. broad. This mineral, called zirkite to distinguish it from another Brazilian mineral baddeleyite, occurs in two forms—rounded pebbles 0.5 to 3 inches in diameter, known under the name Favas in the country, and containing 90 to 93 per cent of zirconia; hard masses, grey to blue-black in colour, and containing 73 to 85 per cent of zirconia. Zirkite seems to contain three distinct minerals—an oxide of zirconium, brazilite, zircon, and another silicate. The deposits which are at present difficult of access are exploited by the Foote Mineral Co., of Philadelphia, who offer a mineral containing 80 per cent of zirconia at £30 a ton, a price which may be expected to fall very considerably in the near future. No rational estimate of the amount of mineral in this deposit has been made, but there seems to be no reason for fearing that it will become exhausted, even if the demand unexpectedly increased. Before the war large quantities of this zirconia were sent to Germany, where its utilisation had been made the subject of many researches.

Before discussing possible applications of zirconia as a refractory product it will be well to enumerate the properties of pure zirconia. It is one of the most refractory substances known; its melting-point would be in the neighbourhood of 3000°. Even when it contains 1.25 per cent of silica and iron oxide it does not fuse below 2500°. The thermal conductivity of the fused pure material is very low, and its coefficient of distillation is low—

* Slightly abridged from *Moniteur Scientifique*, No. 925, 1919, p. 5.

	I.a	I.b	II.	III.	IV.	V.	VI.	VII.
Silica	33.90	29.70	31.36	29.17	30.12	50.36	46.52	7.40
Zirconia	44.85	60.98	20.10	28.96	16.11	15.60	29.33	88.70
Titanic anhydride ..	—	—	6.85	2.00	0.42	—	—	0.60
Tantalum anhydride ..	—	—	—	4.13	—	0.35	—	—
Niobic anhydride ..	—	—	—	—	12.85	—	—	—
Ferric oxide	—	9.20	1.00	0.78	1.26	—	1.40 (Al ₂ O ₃)	4.10
Ferrous oxide	—	—	—	3.02	—	6.37	0.49	—
Manganous oxide ..	—	—	1.39	7.30	1.00	1.61	—	—
Lime	—	—	24.87	6.93	26.95	9.23	4.66	—
Magnesia	—	—	—	—	0.12	—	—	—
Lanthanum oxide ..	—	—	0.33	—	—	—	—	—
Soda	—	—	—	11.23	7.50	13.10	10.06	—
Fluorine	—	—	5.83	3.82	2.98	1.49 (Cl)	—	—
Water	—	—	—	—	—	—	9.05	—
Loss at a red heat ..	—	—	—	0.65	0.74	1.25	—	—
Zircon	—	—	—	3.08	—	—	—	—

I.a Zircon from Ceylon. I.b Zircon from Colorado.

II. Rosenbuschite from Langesund (Norway).

III. Laevenite. IV. Wochlerite from Langesund.

V. Eudyalite from Greenland. VI. Catapleite from Langesund.

VII. Natural zirconia from Brazil.

8.4×10^{-7} , which compares favourably with that of carborundum (6.58×10^{-6}) or alundum (7.1×10^{-8}). Such a substance can naturally be subjected to abrupt changes of temperature without accident. Zirconia is chemically very inert and resists many chemical agents. When heated with silica (in equimolecular proportions) to 3000° , it did not react; the silica simply fused and penetrated the pores of the zirconia. The reaction to which special attention must be directed is its transformation into zirconium carbide when it is heated to a very high temperature in contact with carbon. This is the cause of the destruction of objects made of zirconia when they are heated in an electric furnace, especially in a resistance furnace of granulated carbon. Zirconia, when raised to a sufficiently high temperature, becomes a relatively good conductor. Its specific conductivity, which is 0.0008 at 1200° , becomes 0.0034 at 1400° . This observation is of some practical importance.

It was at the beginning of the twentieth century that articles treating of the utilisation of zirconia as a refractory product began to make their appearance. Until then zirconia was used only for making tablets for oxyhydrogen lighting.

We will first summarise the memoirs published on the subject which seem to us to be the most valuable for the information they give.

The first researches appear to have been carried out at the testing laboratory (Versuchsanstalt) of the Royal Factory at Charlottenburg during 1916. In 1908 Dr. Rieke published the result of researches which he had performed on the use of Brazilian zirconia as a refractory product (*Sprechsaal*, 1908, xli., 214; see also "Natural Zirconia," by Wedekind, *Moniteur Scient.*, 1913, lxxviii., 247). At that time a Hamburg firm had put on the market, under the name Brazilian zirconia, a substance which unlike zircon contained chiefly zirconium oxide. The richest zirconiferous minerals then known corresponded to the silicate (zircon) of formula $ZrSiO_4$, containing a molecule of zirconia combined with a molecule of silica, with a theoretical percentage of 67 per cent as we have said above. The principal impurity was iron oxide, which might amount to 9 per cent. The Brazilian mineral consists chiefly of zirconium oxide associated with iron oxide, alumina, small quantities of titanic anhydride, thoria, free silica, and silica combined with zirconium oxide. The proportion of zirconium varied from 80 to 97 per cent according to the purity. The refractory properties of the mineral are due to the large amount of zirconia it contains.

The first researches were performed with a mineral containing 84 per cent of zirconia, 5 per cent of iron oxide,

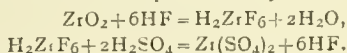
and small quantities of silica, alumina, titanic anhydride, and water. This substance possessed remarkable hardness and a high specific gravity, viz., 5 to 6, while that of the natural silicate lies between 4.5 and 5. Isolated pieces were composed of spherical aggregates having a radiating structure like that of pyrolusite. The colour of the mineral was bluish green; on examination it was seen that there were clear layers and brownish red regions containing oxide of iron. Especially at the surface and in the hollows and depressions there were very ferruginous layers. When isolated fragments were treated for a long time with hot hydrochloric acid the greater part of the iron oxide could be isolated, and the mineral then became a clear brownish grey. This treatment of the mineral in small pieces was insufficient, for it removed only the surface layers of iron oxide; in the interior the coloration remained unchanged. The substance was crushed, and with the aid of flour or starch tubes could be made about 30 cm. long, 6 cm. in external diameter, and 0.5 cm. thick. The contraction on drying was 1 to 2 per cent, that on burning rose to 4 per cent, at the montre 15; the porosity was still fairly great and the colour was brown. The tubes were then employed as heating tubes in a little resistance furnace with granulated carbon. After burning at the montre 30 the porosity was still 3 per cent and the contraction rose to 9 to 10 per cent. At still higher temperatures the surface glazed and little vitreous bubbles were produced; the material then began to conduct, and in order to avoid fusion the temperature was not raised further.

When the material was rapidly cooled cracks were formed. On subjecting it after crushing to treatment with HCl, part of the impurity was removed and the pieces behaved better. With another specimen of the same origin, containing 90 per cent of zirconia and purified with HCl, still better results were obtained. Tubes could be heated up to the montre 41—42, but after a time they became conductors and fused in places. When the still glowing tube was withdrawn breakage occurred and the fused parts sent out sparks. Very probably some carbide had been formed where the carbon had come in contact with the zirconia. The porous structure disappeared on prolonged heating. Crucibles made with the raw mineral broke when rapidly cooled. By making them of mineral which had previously been reduced to large fragments and strongly heated, crucibles which were remarkably resistant to changes of temperature were obtained. No vitrification was observed when they were heated below the montre 30. It may be noted that when in contact with carbon they become more porous after usage in consequence of the volatilisation of the impurities.

These experiments show that the substance, in consequence of its conductivity at a high temperature, is not absolutely suitable for making tubes for granulated carbon furnaces, but on the other hand from its extraordinarily refractory crucibles can be made.

Another experimenter, L. Weiss (*Zeit. Anorg. Chem.*, 1910, lxx., 178), published rather later, in collaboration with R. Lehmann, a series of researches on natural zirconia. The mineral employed in his researches was obtained from Brazil, and was a baddeleyite containing 85 to 93 per cent of zirconia. This product seems identical with (or at any rate of the same origin as) the material used by Rieke. The author also recommends treatment with acid to clean the mineral; he states that the following process gave pure zirconia. He heated in a blast furnace 120 parts of sodium sulphate, 35 parts of carbon, and 100 parts of the mineral with one-third of the weight of sodium chloride as flux. The cooled and powdered mass was taken up with water. The iron was converted into sulphide, titanium into alkaline titanate, alumina into aluminate, and silica into silicate. The soluble salts were filtered off and the residue was treated with HCl or H_2SO_4 , which brought into solution part of the iron, the aluminium, and the titanium. Thus he obtained a substance which was coloured grey owing to the excess of carbon, and which was transformed by calcination into a white mass. If it still contained iron it could be removed by washing with acids.

The author also tried to obtain a still purer zirconia by three other methods. The first consisted in acting on the mineral with calcium fluoride and sulphuric acid, heating for one to one and a half hours. The silica disappears and the titanium partly volatilises; it is then treated with a little cold water, which dissolves the iron, aluminium, and titanium, but hardly any of the zirconium, then a lot of water is added, and the hot liquid is precipitated with potassium carbonate. It is filtered while hot to separate the hydrates of iron, aluminium, and titanium. On concentrating and cooling potassium fluozirconate is deposited. The method of Marignac with fluorhydrate of potassium fluoride can also be recommended. Finally the powdered mineral can be made to react with calcium fluoride and sulphuric acid in an iron tube lined with lead. The reaction can be represented by the equations—



At a high temperature the second equation is complete. Thus large quantities of mineral can be treated with the aid of a relatively small quantity of calcium fluoride.

With zircon the only really useful method is fusion with fluorhydrate of potassium fluoride. If it is necessary not to volatilise titanium and silicon acid sodium sulphate must be used, which acts as well as acid potassium sulphate and prevents the formation of the sulphate of zirconium and potassium.

To obtain zirconia the author uses a rather more complicated method. Two kilograms of the finely powdered mineral are treated with five or six times their weight of acid sodium sulphate; the fused mass is lixiviated and the powdered residue is again fused with bisulphate. Sodium carbonate is added to the green solution until a persistent precipitate is formed; it is then redissolved by sulphuric acid, the solution is separated from sodium sulphate which is deposited, and fractionated by the addition of oxalic acid and ammonia. In order to precipitate the zirconia completely enough oxalic acid must be added to avoid the solution by ammonium oxalate of a double salt of zirconium and ammonium. The last precipitate is pure ferric hydrate. This fractional precipitation is repeated. The purification is ended by transforming into sulphate of zirconium and potassium and precipitating the zirconia by potash, and finally converting into oxychloride. This oxychloride is then evaporated with concentrated sulphuric acid. Ammonium oxalate is added, the solution is electrolysed, ammonium tartrate and ammonia added,

and a current of sulphuretted hydrogen is passed in, which precipitates the iron; it only remains to destroy the organic salts, and zirconia is left.

The author also gives in his memoir a method of analysis of the zirconium minerals of Brazil. It consists in fusing the mineral with acid sodium sulphate. Sulphuretted hydrogen is passed into the aqueous solution to precipitate the platinum which may dissolve, and the silica is eliminated. The latter may retain zirconia, which is recovered by treatment with hydrofluoric acid, and taking up with acid sodium sulphate. The solution from this last treatment is added to the filterings from the silica. Ammonium oxalate and tartrate are added to the solution after neutralisation with ammonia. The iron is precipitated by sulphuretted hydrogen, a little alumina being carried down mechanically. The filtrate is evaporated and calcined, and then taken up with acid sodium sulphate. The solution of the mass after fusion is treated with hydrogen peroxide and the hydrate of zirconia is precipitated by soda, while the titanium remains dissolved as pertitanate.

At the end of this research the author made various attempts to make crucibles by mixing nine parts of zirconia with one of magnesia. As agglomerant he used phosphoric acid in some experiments. By heating the crucibles thus made to 1900° seven-tenths of the phosphoric acid is set free. The author also tried clay. These crucibles showed remarkable powers of resistance, but it is obvious that the process of extraction employed is too costly to be used practically.

The same year Richard Bayer published the result of his researches carried out with zirconia, with the object of making vessels from it. We give here the essential parts of his memoir. The first material used was natural zirconia from Brazil, containing ZrO_2 88.70, SiO_2 7.40, Fe_2O_3 4.10, TiO_2 0.60 per cent.

When this material was powdered and treated with hydrochloric acid 5 per cent of the impurities was dissolved, chiefly iron. The zirconia thus purified still contains 1.86 per cent of iron as ferric oxide. After calcination the iron could be dissolved by treatment with hydrochloric acid, and the zirconia then contained only 1.65 per cent of ferric oxide, and was thus sufficiently pure for a practical experiment. One treatment with sulphuric acid gave a zirconia of the same degree of purity. Various methods of purification have been suggested, without however yielding a remarkably pure product. Lehmann ("Dissertation," Munich) described in detail a process resembling Leblanc's soda process. We have mentioned it above. Afterwards the author recommended the addition of 20 per cent of sodium bisulphate. On lixiviating the mass the silica and titanate acid were brought into solution; the oxides of iron and aluminium were dissolved by subsequent treatment with hydrochloric acid. There remained a grey residue, coloured by excess of carbon, which was transformed by one calcination into a little yellow substance. It contained 0.59 to 1.03 per cent of ferric oxide. The direct process described later is to be preferred to this process, as it yields more easily a purer zirconia.

In practice the zirconia simply purified by acid is usually good enough. Bayer, from whom we have obtained these details, has made a critical study of the methods he had at his disposal for the treatment of zirconia—(i.) Treatment with hydrofluoric acid. (ii.) Transformation into carbide. (iii.) Treatment with sulphuric acid or bisulphates. (iv.) Alkaline fusion.

Of these methods that adopted by Marignac—treatment of the impure zirconia with hydrofluoric acid or its salts—is the best. The mass is fused with three times its weight of acid potassium fluoride, taken up with water to which have been added, on the recommendation of Woebler, some drops of hydrofluoric acid. Fluosilicate of potassium is deposited almost quantitatively; on cooling the liquid colourless crystals of the double fluoride of zirconium and potassium are deposited and

can be brought to a state of perfect purity by recrystallisation. The reaction is quantitative and the yield very good. The zirconia can be extracted from this salt by Hornberger's method, viz., evaporating the fluo-zirconate to dryness with sulphuric acid, dissolving the zirconium sulphate in water, and precipitating with ammonia. The precipitate thus obtained still contains alkalis, so that it must be redissolved and again precipitated. This method, which is suitable for laboratory use and presents no difficulty, cannot be recommended for technical purposes, chiefly in view of the high price of acid potassium fluoride.

(To be continued).

THE ACTION OF ULTRA-VIOLET RAYS ON SUGAR-CANE, PINEAPPLE, AND BANANA, IN HAWAII.

By T. TSUJI.

THE author made a prolonged study of the action of ultra-violet rays on plant physiology. In the paper under review he describes his recent investigations, which show pre-eminently clearly the connection between the action of these rays and the formation of carbohydrates, acids, and other compounds in sugar-cane, pineapple, banana, and other tropical plants.

Sugar-cane.—Perfectly normal sugar-canes were grown in the dark at a temperature of 22° C.; they grew but became pale. Thirty days later they were divided into two lots, one of which was exposed to direct sunlight, the other to ultra-violet rays from a quartz mercury vapour lamp. The etiolated leaves subjected to the action of ultra-violet rays turned a deep green after *two and a half hours*, whereas those exposed simply to sunlight kept their yellow, etiolated colour.

In another experiment three lots of sugar-cane were planted. One was covered with coloured glass (to intercept 50 per cent of the ultra-violet rays of the sunlight), the second was exposed normally to sunlight, and the third to the combined action of the sunlight and that of the mercury vapour lamp. These three lots received equal amounts of fertiliser. After several months the second lot was found to contain 30 per cent more sugar than the first, and the third lot 8 per cent more than the second. The increase in the weight of the sugar of each lot respectively in a given time points to the possibility of reducing the twenty months normally required for each sugar harvest to less than one year by the use of ultra-violet rays.

Pineapple and Banana.—Pineapples exposed to the action of ultra-violet rays ripen more rapidly than those exposed to sunlight only. Pineapples were subjected to the action of ultra-violet rays for forty minutes each morning; the fruit was ripier, more juicy, and larger than that exposed to sunlight only. The same favourable action was observed on the banana. Banana leaves and stalks which had been cut and placed in water kept their original freshness even after two weeks when they had previously been subjected to the action of ultra-violet rays, whereas other untreated material was faded completely after six or seven days. The author sees in this a means of preventing the deterioration of exported bananas, but lays stress on the care necessary in the treatment as the distance, duration, and intensity have to be very carefully regulated to prevent bad effects.

Practical Sources of Ultra-violet Rays.—The ultra-violet rays of sunlight are quickly absorbed by the atmospheric gases, and only a small proportion of them reaches the surface of the earth. The use of mercury lamps is too expensive for practical application. The author, therefore, has attempted to devise more economical methods. In his latest system the ultra-violet rays are derived from small carbon rods impregnated with

sodium tungstate, uranium nitrate, ammonium molybdate, and titanous chloride.—*Louisiana Planter and Sugar Manufacturer*, lx., No. 26.

BRITISH SCIENTIFIC PRODUCTS EXHIBITION, 1919.

THE King has graciously consented to act as President of the British Scientific Products Exhibition, 1919, which will be held at the Central Hall, Westminster, during the month of July. The President of the Exhibition is the Marquess of Crewe, K.G., and Prof. R. A. Gregory is Chairman of the Organising Committee.

The British Science Guild has been encouraged to organise this Exhibition by the success which attended that held at King's College last summer and the more recent Exhibition at Manchester. Now that many inventions can be shown which could not be put before the public during the war, there is every prospect that this year's Exhibition will be even more successful than its predecessors. The objects of the Exhibition will be to illustrate recent progress in British science and invention and to help the establishment and development of new British industries. Such an Exhibition will enable new appliances and devices to be displayed before a large public and will provide progressive manufacturers with an opportunity of examining inventions likely to be of service to them, thus serving as a kind of clearing house for inventors and manufacturers, as well as illustrating developments in science and industry.

The Exhibition will include Sections dealing with Chemistry, Metallurgy, Physics, Agriculture and Foods, Mechanical and Electrical Engineering, Education, Paper, Illustration and Typography, Medicine and Surgery, Fuels, Aircraft, and Textiles. Firms desirous of exhibiting are invited to communicate with the Organising Secretary, Mr. F. S. SPIERS, 82, Victoria Street, London, S.W. 1.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, February 20, 1919.

Sir J. J. THOMSON, President, in the Chair.

THE following papers were read:—

"Dental Changes in the Teeth of the Guinea-pig produced by a Scorbatic Diet." By S. S. ZILVA and E. M. WELLS.

The structure of the teeth of guinea pigs subsisting on a scorbatic diet undergoes radical changes. The ultimate change is characterised by the total disorganisation of the pulp, including the odontoblastic cells. The earliest modification is observed at a period when no other systemic abnormality can be recorded with certainty, and is characterised by the alterations in the odontoblastic cells and the dilatation of the blood vessels of the pulp. Monkeys' teeth are also affected when these animals exist on a scorbatic diet. The bearing of the above results on human subjects is discussed.

"On a New Factor in the Mechanism of Bacterial Infection." By W. E. BULLOCK and W. CRAMER.

The bacteria of gas gangrene (*B. Welchii*, *Vibrio septique*, and *B. edematiens*) and of tetanus, when completely freed from their toxins either by washing or by heating to 80° for half an hour so that spores are formed, do not produce the specific disease when injected into a

mouse or a guinea-pig. The normal animal disposes of the bacteria mainly by lysis and partly also by phagocytosis, and this defensive mechanism is so efficient as to render these bacteria non-pathogenic when injected by themselves.

If a small dose of a soluble ionisable calcium salt is injected together with the bacteria of their spores, the specific disease is elicited in a very virulent form. The chlorides of sodium, potassium, ammonium, strontium, and magnesium, when injected together with *B. Welchii*, are not capable of producing gas gangrene.

A direct contact between the bacteria and the calcium salt is not essential. The phenomenon will occur if the bacterial suspension and the calcium salt are injected at different times into the same site, or into different sites at the same time or at different times.

From these experiments and other experimental evidence the conclusion is drawn that calcium salts when injected subcutaneously produce a local change in the tissues at the site of injection. The effect of this dosage is to bring about a local breaking down of the defensive mechanism against the bacteria of gas gangrene and tetanus. The term "kataphylaxis" is proposed to designate this new phenomenon.

Sterile watery extracts of earth are capable of producing this phenomenon. They may owe this property in many cases entirely to the presence of calcium salts, but there is some evidence that in some cases the extracts of earth owe their kataphylactic action to the presence of another chemical substance or substances, which have not yet been identified.

The bearing of these observations on the etiology of gas gangrene and tetanus is discussed.

"The Distribution of the Serological Types of *B. tetani* in Wounds of Men who received Prophylactic Inoculation, and a Study of the Mechanism of Infection in, and Immunity from, Tetanus." By Major W. J. TULLOCH.

In a previous communication to the Royal Society it was shown that *B. tetani* was susceptible of classification into a number of groups differing one from another in their serological reactions.

As this finding might have an important bearing on the preparation of anti-toxin, as many strains of *B. tetani* as possible were investigated by the agglutination method—

- (i.) From cases of the disease;
- (ii.) From wounds of men showing no evidence of tetanus.

The results obtained show that Type I. bacilli are but relatively infrequently obtained from wounds of inoculated men suffering from tetanus. Thus 19 out of 25 (76 per cent) strains obtained from the wounds of men who showed no evidence of tetanus proved to be Type I. bacilli, while 41 per cent of the strains obtained from men suffering from the disease proved to be of this type.

This observation suggested that there was possibly a mono typical immunity to each serological type, for the serum used for prophylaxis was prepared mainly from the products of Type I. bacilli.

Experiments were undertaken to investigate this question of mono-typical immunity. It was found that—

- (a) Mono-typical anti-toxin neutralises the toxins of all the types.
- (b) Opsonic experiments using mono-typical anti-bacterial sera show that the activity of these is specific in relation to the serological types.
- (c) Experiments undertaken to determine the "anti-infective" value of anti-toxic and anti-bacterial sera suggest, but do not prove, that mono-typical sera protect more adequately against infection with homologous strains than against that with heterologous strains.
- (d) These experiments offered an opportunity of studying the mechanism of infection with *B. tetani*; they indicate that the precise quality, as well as the

degree, of tissue debility, produced by injury, is of importance in initiating the process of infection in tetanus.

- (e) Excretion of wounds appears to minimise the danger of anaërobie infections, but no dressing proved to be of special value in this respect.

INSTITUTE OF CHEMISTRY.

Annual General Meeting, March 3, 1919.

SIR HERBERT JACKSON, the President, referred to the work of the Institute during the war. The record afforded an example of the value to the country of organised professional bodies in times of crisis. The Report contained a concise statement indicating the various directions in which chemists had rendered good service, both with the forces and in industries connected with the war.

The Institute is now co-operating with the Appointments Department of the Ministry of Labour in the resettlement in civil life of those who have been so engaged, and it is hoped that with the return of more normal conditions chemists will be utilised to the fullest benefit in the application of their science to the industries of the country. The President, in referring to the losses sustained by the profession, mentioned especially Lieut.-Col. E. F. Harrison, who will always be remembered for his exceptional work in the provision of means of defence against poisonous gas attacks, to which work he undoubtedly sacrificed his life.

The Institute has before it a period of reconstruction, and will endeavour to bring together in one body the trained and competent chemists both for their own benefit and for that of the community. The Regulations had been modified on such a broad basis that it was hoped all qualified chemists would be able to take part in promoting the welfare of their profession. The Council hoped in the near future to arrange a conference to review the subject of the training for a chemist. Local Sections are being formed in various parts of the country, and the method of the election of the Council will be amended to ensure that its constitution is properly representative of all districts and all branches of professional work. Events of the war have done much to establish the claim of chemists to greater recognition than has been accorded them in the past. The Council have recently prepared a scheme of Government Chemical Service which they hope will secure better conditions for chemists holding appointments under various departments. The vital importance of chemical service to the State had been clearly demonstrated in recent years, and a good example set by the Government would go far to bring home to the public the importance of chemistry to industry and commerce.

The Officers and Members of Council for the ensuing year were elected as follows:—

President—Sir Herbert Jackson, K.B.E., F.R.S.

Vice-Presidents—William Thomas Burgess; Charles Frederick Cross, B.Sc., F.R.S.; Sir James Johnston Dobbie, LL.D., F.R.S.; Gilbert Thomas Morgan, D.Sc., F.R.S.; Sir Robert Robertson, K.B.E., F.R.S.; George Stubbs, O.B.E.

Hon. Treasurer—Edward William Voelcker, A.R.S.M.

Members of Council—William Bacon, B.Sc.; Edward Charles Cyril Raly, F.R.S.; Oscar Lisle Brady, D.Sc.; Francis Howard Carr; Alfred Chaston Chapman; Cecil Howard Cribb, B.Sc.; Alexander Charles Cumming, O.B.E., D.Sc.; Frederick George Donnan, M.A., Ph.D., F.R.S.; John Thomas Dunn, D.Sc.; Alexander Findlay, M.A., D.Sc., Ph.D.; George Watson Gray; Frank William Harbord, C.B.E., A.R.S.M.; Ernest Mostyn Hawkins; Harold George Laell, A.R.C.S.; Joseph Henry Lester, M.Sc.; Frederick James Lloyd; William Macnab; Andrew More, A.R.C.S.; George Henry Perry, M.B.E., B.Sc., A.R.C.S.; Benjamin Dawson Porritt,

M.Sc.; Francis Martin Potter, M.B.E., B.Sc., A.R.C.S.; William Rintoul, O.B.E.; Harry Silvester, B.Sc.; Ernest Woodhouse Smith, D.Sc.; Leonard Ellerton Vhes; Edmund White, B.Sc.; William Maurice Gathorne Young.

NOTICES OF BOOKS.

Aids in the Commercial Analysis of Oils, Fats and their Commercial Products. By GEORGE FENWICK PICKERING. London: Charles Griffin and Co., Ltd. Pp. vii + 133. Price 7s. 6d. net.

THE methods described in this book are those which have been found most useful in works' laboratories, and the author's extensive experience in the analysis of fats and oils enables him to give much information which is not to be found elsewhere. All the figures given are published for the first time, and throughout the book great care has been taken to state precisely what standard of accuracy is to be aimed at. The author's advice is thoroughly practical and reliable, and he not only gives full details as to the procedure which is to be adopted in various cases, but he also points out what not to do, and how to avoid error in carrying out the tests. The examination of the physical and chemical properties of oils and fats in general is first discussed, and statistics and data are given in sufficient number to enable the chemist to decide as to the purity of any given sample. The qualitative detection of different oils is then described very fully and completely, a comparatively long chapter being devoted to glycerine and a full account being given of methods of examination of recovered products. For chemists engaged in oil analysis no more useful and concise laboratory guide could be found.

BOOKS RECEIVED.

- "Statistics of the Synthetic Dyestuffs imported into the United Kingdom during the year 1913. Pp. x + 168. Printed under the Authority of His Majesty's Stationery Office.
- "The Bulletin of the Federation of British Industries." Lyons Fair Edition. Pp. 122.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Enrolith.—A correspondent is anxious for information as to sources of supply of this material, and will be grateful if any reader will provide him with the same.

MEETINGS FOR THE WEEK.

- MONDAY, 10th.—Royal Society of Arts, 4.30. (Caator Lectures). "Coal and its Conservation," by Prof. W. A. Bone.
- Ceramic Society, 7. "In the Central Schools of Science and Technology, Stoke-on-Trent." "Nigerian Pottery," by D. Roberts.
- TUESDAY, 11th.—Royal Institution, 3. "Insect Problems," by Prof. H. Maxwell-Lefroy.
- WEDNESDAY, 12th.—Royal Society of Arts, 4.30. "Electric Welding and its Applications," by W. L. Lorkin.
- THURSDAY, 13th.—Royal Institution, 3. "Whistler and Sargent," by Charles Anken.
- Royal Society of Arts, 4.30. "The Report of the Indian Industrial Commission," by D. T. Chadwick.
- Royal Society, 4.30.
- FRIDAY, 14th.—Royal Institution, 5.30. "The Organ of Hearing from a New Point of View," by Prof. A. Keith.
- SATURDAY, 15th.—Royal Institution, 3. "Spectrum Analysis and its Application to Atomic Structure," by Prof. Sir J. J. Thomson, O.M.

Royal Institution.—Captain Thomson will deliver his postponed lecture on "The Dynamics of Flying" at the Royal Institution on Monday, March 10, at 3 o'clock.

Assistant, aged 21 to 24 years, required in Analyst's Laboratory.—Write, giving particulars of experience, &c., to O. A., care of Street's, 30, Corohill, E.C. 3.

Assistant Analyst (Woman), four years' experience in General Analytical Laboratory (Foods, Brewing-sugars and Malts, Chemicals, &c.), desires London permanency. Matriculated with Chemistry. Salary £150.—Address, V. A. H., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Demobilised Cadet (19) requires Situation in Laboratory. Good all round education; Public School. Passed Inter. B.Sc. One year's previous experience.—Address, J. C. H., 23, Westcott Street, Hull.

French Young Man, aged 20 (French Baccalaureate Sc. Phil.), requires Employment in Chemical Works or Laboratory.—Address, J. M. Lerpette, 22, Rue des Guettries, Tours (T. es L.), France.

Works Analytical Chemist required. One conversant with Soap Manufacture, Nicotine Extractions, and Agricultural and Horticultural Preparations. State full particulars and salary required.—Address, W. A., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

FOR SALE.

Case of MATERIA MEDICA SPECIMENS for Pharmaceutical Students, PROCEEDINGS OF ROYAL SOCIETY, Series B, 1910-13. Also PHILOSOPHICAL TRANSACTIONS. BIOCHEMICAL JOURNAL, 1913-7. JOURNAL OF CHEMICAL SOCIETY, PROCEEDINGS, and ANNUAL REPORTS, 1912-18. CHEMICAL NEWS, 1907-9.—Address, "Westdean," 59, York Road, Aldershot.

BATTERSEA POLYTECHNIC, London, S.W. 11.

The Governing Body invite applications for the Position of PRINCIPAL of the Polytechnic. The commencing salary of this appointment will range from £800 to £1000 a year, according to qualifications, and will rise by annual increments of £20 to a maximum of £1000 a year. The appointment will date from September 1st next.

Applications must be received on or before SATURDAY, APRIL 5th next.

For particulars apply at once to the Clerk to the Governing Body, Battersea Polytechnic, S.W. 11.

LINEN INDUSTRY RESEARCH ASSOCIATION.

Applications are invited for the Post of DIRECTOR OF RESEARCH for the Linen Industry Research Association.

Candidates should state their Scientific and other qualifications, such as administrative, industrial, &c., and furnish the names of three references.

The functions of the selected candidate will be to make a survey of the entire field of Research in the Linen Industry from the growing of the flax to the completion of the finished product, to draw up a programme of Research, to organise the scheme, and to supervise its carrying out.

A salary of not less than £1000 a year is offered.

Further particulars and the Prospectus of the Association may be obtained from the SECRETARY, 3, Bedford Street, Belfast.

PORTSMOUTH MUNICIPAL COLLEGE.

Principal—OLIVER FREEMAN, Wh.Sc., A.R.C.S., B.Sc.

APPOINTMENT OF LECTURER IN CHEMISTRY.

Applications are invited for the Position of a LECTURER IN CHEMISTRY at the Portsmouth Municipal College.

Salary from £200 to £300 per annum, according to qualifications and experience.

Application Forms and further particulars may be obtained by forwarding a stamped addressed foolscap envelope to the SECRETARY, Offices for Higher Education, The Municipal College, Portsmouth, to whom applications should be returned, accompanied by copies of not more than three recent testimonials, at once.

H. E. CURTIS, Secretary.

THE CHEMICAL NEWS

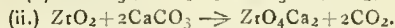
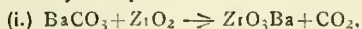
VOL. CXVIII., No. 3074.

ZIRCONIA: ITS UTILISATION AS A REFRACTORY SUBSTANCE, AN OPACIFIER, AND AN ABRASIVE.*

By M. A. GRANGER.

(Concluded from p. 118).

VARIOUS workers—Troost, Moissan and Lengfel, Wedekind among others—have shown that zirconia is transformed quantitatively into carbide in the electric furnace, when it is heated with carbon, and according to Wedekind the reaction is facilitated by the addition of lime. This carbide of zirconium is fairly stable; it is only slightly attacked even by aqua regia. Owing to the high temperature employed the most important impurities, such as iron and silica, are almost completely volatilised. Lehrmann suggested heating the carbide in an oxidising atmosphere; then carbon remains as graphite, and can be removed by levigation. The oxide of zirconium thus obtained still contains about 0.18 per cent of ferric oxide. One single treatment with sulphuric acid or bisulphates is never sufficient, even when the mineral has previously been brought into a very fine state of division. Treatment with alkaline carbonates, with or without the addition of nitrate, and fusion with alkalis lead to the same result. In every case the mass became too fluid considerably below the temperature at which the reagents could act on the zirconia, so that the mineral fell to the bottom of the crucible and did not mix with the flux. This led to an attempt to extract the zirconia with a difficultly fusible alkaline earth carbonate. Very few data relative to the extraction of zirconia by alkaline carbonates have been published. Berthier is the only one who has extracted zirconia by fusing iron in a carbon crucible with quartz and marble (zircon, 10; quartz, 3.3; marble, 11.1). The iron must be reduced and serves as a metallic regulus. Wedekind used chalk to bring about the transformation into carbide. The alkaline earth did not act as a reagent, but was transformed into carbide, which accelerated the formation of zirconium carbide. Barium carbonate has been used, because at the high temperature necessary for the reduction this salt is not transformed into oxide. The reaction may be represented as follows:—



The author has not investigated which is the chief of these two reactions; in order to be sure of having carbonate present in excess he calculated on the basis of Equation (ii.), and used four times the weight of barium carbonate. The mixture was heated for half-an-hour to 1400° in a platinum crucible, and then kept at this temperature for another half-hour. The reaction is quantitative if this procedure is followed. It is not advisable to heat too strongly; in consequence of low conductivity the agglomerated mass would contain an unattacked nucleus. Then the mass is treated with hydrochloric acid diluted with two volumes of water. It is evaporated to dryness to separate the silica. The residue is taken up with dilute hydrochloric acid. A small quantity of zirconium oxychloride is retained by the silica, and the zirconia in solution retains a small quantity of silica (about 0.2 per cent). The chief difficulty is due to the removal of iron. Berthier and Woehler suggested transforming the iron into sulphide and acting with sulphurous acid. Hermann and Stromeier precipitated the zirconia

with sodium hyposulphite. Dietrich and Freund prefer to treat the iron in solution in a weak mineral acid and to heat in absence of air with a solution of sodium acetate, which precipitates the hydrate of zirconia. Bailly precipitated the zirconia with peroxide of hydrogen in acid solution, the iron remaining dissolved. Geisow and Horckheimer made the solution alkaline and added hydrogen peroxide to keep the zirconia. Hillebrand precipitates the zirconia in a feebly acid solution by hydrogen peroxide and disodium phosphate. Dubois and Silveira, and also Woehler, dissolve in oxalic acid the oxide of iron contained in the precipitate which ammonia gives. Berzelius separates the zirconium as double sulphate by adding a hot concentrated solution of potassium sulphate. Seidel gives the preference to precipitation as fluoride. Hanser dissolves the sulphate obtained by heating the mineral till no more fumes are evolved with concentrated sulphuric acid, and then diluting with much water, when a basic precipitate is obtained containing 66.7 per cent of the zirconia present.

The most complete separation is effected by adopting the method of Berzelius as modified by Wedekind. After the addition of tartaric acid the iron is quantitatively precipitated without a trace of zirconia in ammoniacal solution by means of sulphuretted hydrogen. This method is useful in analysis, but is not applicable for a commercial separation owing to the cost of tartaric acid and the complicated later treatment of the solution. The most convenient method is that of Wedekind, based upon the fractional crystallisation of the zirconia as oxychloride in solution in hydrochloric acid. Barium does not interfere with this reaction. The first crystallisations contain most of it, but the last only slight traces. This barium, which adulterates the oxychloride, can easily be removed after the transformation of oxychloride into hydroxide. The crystals are dissolved in water, the solution is precipitated whilst hot with ammonia, and the hydrate of zirconia thus obtained is washed by decantation. It is then calcined to convert it into zirconia. The zirconia thus obtained is very pure; alumina and titania remain with iron oxide in the mother-liquor.

In order to obtain information as to the practical utilisation of the process Brazilian zirconia was first treated with hydrochloric acid, and 700 grms. of this product were mixed with 2800 grms. of barium carbonate. The whole was heated in a plumbago crucible in a blow-pipe furnace for an hour without success. In order to obtain any result a long and steady heating is required, like that of an earthenware or porcelain furnace.

By using the method of separation described above a hydrate of zirconia was obtained and transferred to a filter-press. This hydrate forms a jelly which is difficult to wash and to filter and contains only 8 per cent of ZrO_2 . The yield was 80 per cent, giving 4.97 per cent anhydrous zirconia. This zirconia contained as impurity 0.19 to 0.325 per cent of silica, a little less than 0.01 per cent of iron oxide, and no titania.

To make vessels of zirconia a binding material is necessary, and the use of zirconia hydrate has been tried for the purpose. (H. S. Claire-Deville suggested an analogous method for making crucibles of alumina). The vessels were so fragile that another binding material had to be found. Starch is specially appropriate. It was intimately mixed with the hydrate and allowed to dry in the air for some hours until it contained 9 to 10 per cent of zirconia (calculated as ZrO_2). This addition produces no ill effects, as starch burns easily at a red heat. The gelatinous hydrate mixed with the calcined hydrate or with Brazilian zirconia simply purified by treatment with hydrochloric acid gave a mass which could be kneaded. After several experiments it was found that plaster moistened with a little water makes the best mould. The damping was designed to prevent too rapid desiccation; for the same purpose the mould could be covered with a layer of graphite. To make the hollow a core of wood covered with tin-foil was used, kept exactly in the centre

* Slightly abridged from *Moniteur Scientifique*, No. 925, 1919, p. 5.

of the mass by a vertical bar. The tin-foil was removed by means of a small pair of pincers. After two hours the vessel could be lifted from the mould. It was allowed to dry for a day in damp air and for the same time in dry air and then at 50° and 100°. Finally it was raised to a red heat and baked.

These experiments showed that ordinary baking was not sufficient for zirconia crucibles, as might be foreseen from the properties of zirconia. Some crucibles were baked at considerably higher temperatures, such as those obtained with a Hempel resistance furnace. Thus 2000–2300° could be reached. In these conditions remarkable results were obtained; the crucibles which had till then been very friable became very decidedly solid. Crucibles of pure zirconia revealed a superficial formation of carbide which made them fragile; it is probable that the temperature was still too low, but it is also possible that in order to make it bind traces of iron and silica are necessary.

These crucibles of raw zirconia, which were resistant to chemical action and were not attacked by reagents, were also remarkably resistant towards abrupt changes of temperature. They could be heated rapidly in a blowpipe flame, and when incandescent could be plunged into water without being damaged. It was particularly interesting to be able to determine the melting-point of the material used for making these crucibles. It is difficult to give details, for the only source which could be used was the flame of the electric arc. As a guide it may be said that this refractory material would stand 2300° without accident.

Zirconia is thus one of the most refractory substances known, and only carbon would surpass it, but zirconia would have the advantage of usually being very slightly reactive. Zirconia is the only insulator which can resist a current of average tension up to 2000°. (This is in contradiction to the results of Rieke and my own observations).

The author concludes his article by quoting the Allgemeine Elektrizitäts Gesellschaft of Berlin, as having manufactured crucibles of agglomerated zirconia with a composition which was kept secret, but which would leave a residue of 0.38 per cent of magnesia and 4.15 per cent of potash and soda.

J. A. Audley has made some interesting observations on the subject of the employment of zirconia (*Trans. Am. Ceramic Soc.*, 1916, xvi., 121). The first material which he employed was baddeleyite; it contained 82 to 94 per cent of zirconium oxide, and he also used Brazilian zircon coming from monazite sands. He fused the zirconia in an electric furnace, consuming 300 ampères at 70 volts. He made bricks with raw baddeleyite agglomerated with a little clay, and he showed that these bricks resisted a temperature of 1650° provided that they had been baked at a higher temperature; otherwise they split. The use of material which had been treated with a dilute acid to extract the oxide of iron gave better results. He also made crucibles with a binding material such as glucine, alumina, thorium, and yttria, provided that he did not introduce more than 1 per cent. Silica and magnesia could not be used because they volatilise at about 2000°. These crucibles, when heated to 2000°, acquire a crystalline structure, and keep their shape to 2400° if the heating is regular. Though harder and more compact than clay crucibles they carbonise readily, and could not be used more than three times. When the natural substance was used for making the crucibles they became covered with bubbles below 2000°. If the crucibles were well made and were subjected to prolonged heating a loss of weight was observed owing to the reduction of the zirconia to a lower oxide, the formation of carbide, and the volatilisation of the oxides added, and the zirconia. Finally, the crucibles broke owing to the transformations produced by the successive oxidations and reductions of the mass. Among other authors we must mention Raff (*Zeit. Anorg. Chem.*, 1914, xxxvi., 864; 1916, xcvi., 73) and Podszus (*Zeit.*

Angew. Chem., 1917, xxx., 17), who also published articles on experiments with zirconia, without, however, giving any more valuable information than their predecessors. Raff tried magnesia as binding material and additions of rare earths. His observations confirm the facts already described. Podszus also published a memoir, the most interesting results in which related to the use of fused zirconia. He described a furnace of fused zirconia, heated by an oxyhydrogen flame, and capable of being raised to 2500°.

Hitherto we have dealt only with laboratory researches, and if the employment of zirconia could have no development outside this restricted sphere we should not have called the attention of our readers to it. The first article, as far as I know, which gave information relating to the practical employment of zirconia was published by Meyer in 1913 (*Metal. Chem. Eng.*, 1914, xii., 191; 1915, xiii., 362). The author pointed out the possibility of making a refractory material by using a natural mineral containing:—Zirconia, 84 per cent; silica, 8 per cent; ferric oxide, 3 per cent. Experiments carried out in a Martin furnace, at a steelworks at Remscheid, in Germany, showed that a covering of zirconia lasts a long time, and that in spite of the decidedly higher initial cost there is still a saving of 50 per cent. A covering of zirconia may last eight months, and give an increased production which increases the yield. Its conductivity is only half that of a refractory brick.

In metallurgy zirconia could also be employed in the preparation of copper and its alloys. The only corrosive agents are fluorides and acid sulphates. The difficulty, putting aside the question of cost, depends on the method of employment. Silicate of soda and tar are used for the coverings. Zirconia can be used with tar if the heating is performed very slowly. Lime employed in very small quantities would also give good results if utilised with discretion. Meyer calculates that the amount necessary for the covering of a Martin furnace is 900 pounds, which at 7 cents a pound comes to 63 dols., and represents a considerable saving over covering with refractory bricks.

In every case before the war Germany had tried to lay their hands on the deposits of natural zirconia; it seems that they had foreseen developments in the case of this product.

Having need of a refractory material which would be capable of resisting at least the temperature of fusion of platinum I undertook experiments on refractory products, a summary of which I will give here, as far as zirconia is concerned.

There could be no doubt of using pure commercial zirconia owing to its high price, and I had to have recourse to the natural products. The mineral which I had at my disposal was zircon, delivered to me in the form of a yellow powder.

The work already done when I began my researches seemed to be worth verifying if I limited myself to the point of view which interested me. Zircon, treated with hydrochloric acid, gave up iron which enabled its refractory qualities to be improved. By pressure I could obtain little crucibles and briquettes, using as agglomerants lime, silicate of soda, or organic binding materials. Meyer in the memoir quoted above gave as a composition binding well:—

Zirconia, mesh	100	75
"	10	23
Lime	—	2

Three per cent of silicates of soda was added at 38°. The moulded and dried products must be burnt at 1400°. This composition answers very well for anything that could be pressed, and I obtained satisfactory results, either using it unaltered or by modifying it. As I wished to use a tubular furnace I had first to experiment with zirconia as a refractory material. The preceding composition is in no way suited to the moulding of a tube, and at the expense of the refractory properties I tried to

mould tubes by agglomerating the natural product with a very refractory clay-like Mussidan clay. The result was not satisfactory. When using these tubes in a granular carbon resistance furnace I found, in agreement with Ricke and in contradiction to the assertions of Baeyer, that the tube when once hot became a conductor, the ampère rose rapidly, then a helical arc was produced throughout the length of the tube, and the latter soon became corroded. When it cooled it was examined, and was found to be red-brown, the structure was vitreous, and the mass was fissured and brittle. In face of this result it was useless to continue the experiments even with a purer product. As regards the crucibles it was not the same. Purified zirconia gives excellent crucibles, which it is best to shape in a press with an organic binding material. In spite of Baeyer's opinion I have found that it is easy to obtain a sufficiently pure zirconia for making crucibles by treating zircon with sulphuric acid. It is sufficient to grind the mineral very fine and to heat it on a sand-bath with concentrated sulphuric acid (after a preliminary treatment with hydrochloric acid). It is the process which requires the least manipulation if one is limited to a product of normal purity. The solution is evaporated to dryness and taken up with water. The zirconia can be extracted from this sulphuric solution by the following different processes:—The acid solution diluted with water precipitates a basic sulphate; the addition of potassium sulphate precipitates a double sulphate; the addition of ammonia precipitates hydrated zirconia; the calcination of the sulphate or hydrate of zirconium gives zirconia. The third method would be the simplest if the filtration and washing of the hydrate were not troublesome. It is important to use only strongly calcined zirconia, otherwise the articles will contract considerably.

Summarising, my results agree with those of Ricke as regards the utilisation of zirconia in experiments at high temperatures. I have also shown that the natural product agglomerates easily by pressure, and the making of coverings of zirconia presents no more difficulty than the moulding of inert substances. Like stannic oxide, SnO_2 , a certain number of oxides (especially of tetra-valent elements), such as ZrO_2 , can play the part of opacifiers in fluxes for enamels and glasses. I have not been able to find out for certain who first thought of using zirconia as an opacifier. Hillringhaus and Heilemann (*Zeit. Anorg. Chem.*, 1910, lxvi., 436), following on the work of Weiss and Lehmann, suggested the possibility of using zirconia as an opacifier in consequence of the rise of tin. These authors draw attention to the fact that the firm of Gustrow in D.R.P. 189364 have claimed a method of preparation of glasses opacified by zirconia. Laudan and Rosensweig also claim the employment of zirconia with or without glucine as an opacifier (B.F. 389483—1908). Unless we can obtain zirconia free from iron and at a price competing with that of tin or antimony oxide I do not see what real interest there can be in the numerous patents taken out by various authors. For ten years several patents have been taken out annually dealing with the preparation of enamels opacified by zirconia. According to Grünwald (*Spektsaal*, 1911, xlv., 72, No. 5) all the substances proposed for replacing tin oxide, such as titanin anhydride or zirconia, have not been very successful. The following enamel has been suggested:—

Felspar	37.5
Borax	18
Saltpetre	0.7
Zirconia	8
Cryolith	21
Quartz	10.5
Zirconia (to be added to broken mass)	6
Clay	7

Such an enamel would not have a considerable covering power, and the inclusion of 14 per cent of zirconia would raise the price considerably. Moreover a large amount of

cryolith is required. I do not think that the subject has made much progress at present. The only interesting development would be that according to some workers an enamel could be obtained which would be remarkably resistant to acids. In order to form an opinion it would be necessary to know the results of the use in practice of vessels covered with an enamel made to satisfy the conditions of resistance which are met with in industrial processes and not in laboratory tests. Zirconia has also been used in glasses. This subject having already been discussed ("Le Siloxide, Sucédané du verre de quartz," Félix Thomas, 1912, lxxvii., 790) we need not return to it here.

A final possibility in the employment of zirconia may be mentioned, namely, the use of zircon as an abrasive, in view of its hardness. Grindstones of zircon, agglomerated in the cold, have given good results in working mother-of-pearl. This would perhaps provide a small outlet for zircon. As zircon is not unalterable in the presence of silicates it cannot be used for making ceramic grindstones, that is to say grindstones in which the binding material is a silicated compound fusible at a high temperature. It can only be used in cement grindstones.

The value of zirconia as a metallurgical refractory product seems to be firmly established as the result of these investigations.

RELATIONSHIPS IN CHEMISTRY.*

By J. W. BECKMAN.

THERE are some matters which have impressed themselves upon me during the last year most emphatically which I wish to present and so bring them to your attention and serious thought.

To make myself clear in the following discussion, I am going to take the liberty of classifying chemists under two heads: The inside chemist, to which class, in a general way, belongs the man engaged in chemical work in the university, not including the student; and the outside chemist, to which class belong all other chemists occupied in practical application and research in chemistry. This is, as you fully understand, not a hard and fast classification; the different groups naturally overlap.

There was a time, and it was not long ago, when there was, I believe, a feeling existing between the outside chemist and the inside chemist. It was not one that was distinctly tangible or that could be attributed to any special reason or that had any just cause.

The inside chemist, whose duty primarily consists in continuing to bring forth new generations of chemists, was liable to look upon his own offspring as a being somewhat inferior to himself; his offspring had only glanced through frosted windows into the holy of holies of theoretical chemistry. The young chemist had spent too short a time, as a rule, in the university, in the atmosphere of the inside chemist, to absorb more than a smattering, in many cases, of the deeper meaning of chemical laws. These embryo chemists formed later the increasingly growing number of outside chemists. It was therefore natural that the feeling on the part of the inside chemist of contempt for and of superiority to the outside chemist was continued in an unabated stream. There was a tendency among the inside chemists to look upon their work as a sacred work, a work which gave them mental stimulus, and which at times perhaps gave them mental bliss. As an opiate fiend obtains physical bliss from his narcotic, so the inside chemist got intellectual bliss from his intellectual narcotic. From time to time, as a miser will of a night take out his gold and let it trickle through his fingers and again lock it up and enjoy this pleasure, so

* Address delivered at the 1918 annual meeting of the California Section of the American Chemical Society.

would the inside chemist from time to time take out the precious discoveries he has made and ventilate them in an abstract way, and again lock them into the sanctuaries of his research.

The outside chemist, as I have stated before, is really a product of the inside chemist. As time went on and the influences which he had absorbed in the university gradually were rubbed off in the hard outside world and he was brought face to face with the realities in life and in chemistry, he began to look back upon the inside chemist with somewhat of a naïve contempt.

Because the inside chemist dealt with complex laws and theories in chemistry and the outside chemist dealt, in many cases, with pipes and tanks, and weights of solutions, &c., the outside chemist began to estimate himself as the most important man because he was dealing with more tangible things; he began to look down upon the inside chemist with a feeling of superiority and thought that the inside chemist was an unpractical old fogey.

Each seemed inclined to go his own way. The inside chemist was not interested as to how his discoveries could help the outside chemist, excepting in so far as he might sow some seeds regarding his discoveries in the new generation of chemists. The outside chemist, who had grown away from the inside chemist's influence, had a hard time in many cases to absorb, or reasonably understand, the discussions he might have had with the inside chemist along the lines of the latter's discoveries—discussions which might have been to their mutual advantage—and his final analysis was that they did not concern him in his special activities anyway.

I may have drawn my picture somewhat harshly, but I think that we all recognise the fact that there did exist a degree of lack of understanding between the inside chemist and the outside chemist.

The war in its activities has wrought, I believe, a very radical change in the attitude of the two chemists, and it is a change which is to everyone's advantage and one that is of vital importance to the chemical development of the country, and for that reason, if for no other, should be maintained and encouraged in every way.

Through dire necessity the outside chemist has been forced to seek out the inside chemist and get his advanced viewpoints on many of the apparently most simple chemical processes of manufacture, for the purpose of speeding up war work, increasing efficiency, and avoiding waste. The inside chemist may never have known anything about valves and pipes, kettles, and other things, excepting possibly in the abstract, but he has, through his careful research and through his trained mental capacities, a fountain of information, which, unlocked and coupled with the practical knowledge of the outside chemist, has contributed to the chemical development of the country in a manner which has brought results, in a few years, undreamed of as being possible to achieve under conditions as they existed before. In other words, the inside chemist and the outside chemist have finally met on the same ground; they have been called to the same council chamber and have been forced to discuss together problems of vital importance to the national welfare in a language that both of them understood. The outside chemist may often have had a hard time to put his ideas and his observations into terminology which was not offensive to the trained ear and mode of expression of the inside chemist, while the inside chemist may equally well have had a hard time to express his viewpoints and his ideas in the language which was acceptable and easily understood by the outside chemist; but they have done it, as shown by the surprising and marvellous results of the last few years.

The inside and the outside chemist have joined hands and have learned to speak the same language, both of them perhaps still falteringly, but it is accomplished, and as time goes on, the inside chemist will realise that any discovery which he may make and which he keeps locked

up as a miser keeps his gold locked up, without trying to see whether it will better conditions in the outside world, is a useless discovery and his time is wasted and he himself might be considered as lacking in morality.

The same may be said of the outside chemist. If the outside chemist, through sheer stubbornness, through lack of perseverance, and through ignorance, is unwilling to give an ear to the inside chemist's advice, he shows himself morally unfit to further the chemical development of the country.

I am fully convinced that a new generation of chemists is going to grow up from now on as a result of the war. The outside chemists, who are the offspring of the inside chemists, will be no more and the inside chemists will be equally eliminated. We will have a new type with a broader viewpoint in all these matters. We will look to the theoretical chemist with regard and appreciation equal to that which we show the technical and applied chemist. Our chemical development will die out just as quickly as it has grown if we are unwilling to continue to appreciate the fact that all chemists are interdependent, that chemistry is not chemistry without theoretical foundation, and that theoretical knowledge is worthless to man without its application in some way for his improvement.

My feeling is that the meetings of the Local Sections of the American Chemical Society, such as we attend to-night, are of the greatest importance to our future chemical development. The men who interest themselves primarily in the applied chemistry should make an effort to follow the discoveries of those chemists who read papers on theoretical chemistry and discuss them in the meetings. It may sometimes be a mental effort to do so, but it is worth while, while the theoretical men should take equal interest in discussing papers on applied chemistry, bringing their viewpoints and their buried theoretical knowledge to the vision of the applied chemist. There should be a feeling of give-and-take at such discussions. It should not be a disgrace for a man to show his ignorance in theoretical chemistry, nor should it be a disgrace for a theorist to show his ignorance as to applied chemistry. We do not live in the days of Michael Angelo and consequently it is impossible for us all to be able even to discuss all the different sides of our own science faultlessly and always intelligently.

It occurs to me to ask in this connection, if we are not making a mistake, as a Society, in having two publications, one of them publishing matters dealing with applied chemistry, and the other one dealing with theoretical chemistry. Should we not, as a Society, show our belief in the unity of chemistry by issuing one single journal dealing with chemistry as a whole? As it is now, the theoretical chemist reads the *Journal of the American Chemical Society* and lays aside, unread, the *Journal of Industrial and Engineering Chemistry*, and the chemist interested in applied chemistry reads only the *Journal of Industrial and Engineering Chemistry* and puts aside the *Journal of the American Chemical Society* unread. My belief is that if these journals were published jointly in the same volume, we would be forced to glance over all the articles occurring in it, and the line of demarcation between applied chemistry and theoretical chemistry would be quickly eliminated.

We have on the Pacific Coast, I believe, a special responsibility to each other. We are far from the large centres of chemical activity and consequently are thrown more intimately together. We will have to learn to depend much more on each other than we have done up to the present time. The war has brought with it many worries and troubles, but has also helped us, in many cases, to clarify our viewpoints and put new stimulus and new understanding into our efforts. Our development out here, if it is going to increase at all and be successful, is dependent on a most intimate co-operation and understanding between all the different branches of chemistry and its application.—*Journal of Industrial and Engineering Chemistry*, xi, No. 2.

THE INORGANIC CONSTITUENTS OF LOBSTER SHELLS.*

By FRANK WIGGLESWORTH CLARKE and
GEORGE STEIGER.

IN the course of an extensive investigation relative to the inorganic constituents of marine invertebrates, by Clarke and Wheeler (Prof. Paper, No. 102, U.S. Geological Survey, Washington), it was found that among the distinctly magnesium organisms the proportion of magnesia was dependent upon the temperature of the water in which the animals live. The cold water animals contained much less magnesium carbonate than those from warm waters; a relation which was strikingly manifest in the analyses of echinoderms and alcyonarians and which has been amply verified by a considerable number of new analyses made since the original memoir was published. In other groups of organisms the same relation was suggested, but not actually proved to hold, for there were exceptions that needed explanation. In a series of eleven analyses of crustaceans (crabs, lobsters, shrimps, &c.), the same variation in magnesia was strongly indicated, but with irregularities which appeared to require further investigation. It was conceivable that different parts of a shell or skeleton might differ in composition, or else that variations might be due to differences in age. It had already been found in the case of two sea urchins that the spines contained much less magnesia than the main body of the shells, but the question relative to age remained to be investigated.

Through the kindness of Dr. H. M. Smith, director of the U.S. Bureau of Fisheries, the large claws of two lobsters (*Homarus americanus*) from a single locality, Boothbay Harbor, Maine, were obtained, one from a small lobster, the other from a large specimen. The analyses gave the following results, after rejecting organic matter and water and recalculating to 100 per cent:—

	Small Lobster.	Large Lobster.
SiO ₂ + (Al, Fe ₂) ₂ O ₃	0.19	0.81
MgCO ₃	6.02	11.51
CaCO ₃	80.52	64.37
CaSO ₄	1.29	1.85
Ca ₃ P ₂ O ₈	11.98	21.46
	100.00	100.00

The difference between these two analyses is very great, the large animal being much more highly magnesian and phosphatic than the small one. Unfortunately, however, the actual sizes of the two lobsters were not given, and more precise data were evidently desirable. Accordingly Dr. Smith had fragments from three lobsters sent to us, all from the same station as the others, with definite figures as to length and weight. The fragments, moreover, in each case represented both the large claw and the carapace, so that variations in the individual as well as variations in age could be determined. The analyses, six in number, were as follows:—

1. Small lobster, length 8½ inches, weight 10 ounces.
 2. Medium lobster, length 11½ inches, weight 2 pounds.
 3. Large lobster, length 16½ inches, weight 5½ pounds.
- The claw is indicated by *a*, the carapace by *b*.

	1a.	1b.	2a.	2b.	3a.	3b.
SiO ₂ + (Al, Fe) ₂ O ₃ ..	0.33	0.35	0.36	0.66	0.34	0.57
MgCO ₃	10.81	7.74	11.28	8.12	10.99	8.77
CaCO ₃	72.41	78.98	55.46	70.58	56.89	65.14
CaSO ₄	1.24	1.23	2.12	1.58	2.32	2.32
Ca ₃ P ₂ O ₈	15.21	11.70	30.78	19.06	29.49	23.20
	100.00	100.00	100.00	100.00	100.00	100.00

In each case the claw is richer in magnesium carbonate and calcium phosphate than the carapace. The variations due to age appear more distinctly when the average of each pair of analyses is taken, as follows:—

	1	2	3
MgCO ₃ ..	9.27	9.70	9.88
CaCO ₃ ..	75.69	68.02	61.01
Ca ₃ P ₂ O ₈ ..	13.45	24.92	26.35
CaSO ₄ ..	1.24	1.85	2.32

Here the progressive increase in magnesium carbonate and calcium phosphate is clearly shown; and it also appears in the percentages of calcium sulphate, although the last detail is less significant. The smallest lobster, moreover, differs in the composition of its inorganic portion from that of the two larger animals much more than they do from each other.

From the evidence now at hand it seems clear that some of the departures from regularity in the proportions of magnesium carbonate in the shells or skeletons of marine invertebrates are due to one or both of the two causes which were suggested at the beginning of this paper. It is desirable, therefore, in further investigations of this kind that in the study of the more highly specialised organisms the analyses should represent the totality of the inorganic portions, and that animals of the same degree of maturity should be taken. With the lower classes of organisms the difficulties are not so great, and regularities are much more easily discovered.—*Proceedings of the National Academy of Sciences, U.S.A., v., No. 1.*

TWO NEW ZIRCON MINERALS—ORVILLITE AND OLIVEIRAITE.*

By T. H. LEE, F.C.S., Lond., N.Am.C.Soc.

1. Orvillite.

YEAR before last there came to the Serviço Geológico e Mineralógico do Brazil a number of specimens of a zirconiferous rock from the region of Caldas, in the State of Minas Geraes. Several of them were almost entirely of the oxide of zirconium known as baddeleyite (brazilitite of Hussak), and some of them contained 92 per cent of the oxide of zirconium.

When Orville A. Derby, the lamented director of the Survey, received this material he began a study of it with a view to proposing the name "caldasite" for the rock itself, so that the name baddeleyite would be restricted to the crystalline oxide of zirconium, and thus preventing the use of the name of the mineral for that of the rock. And as it is typical of the region of Caldas, its origin would thus be indicated.

Among the many varieties of this rock are some that have cavities filled with small crystals of silicate of zirconium (zirconite). By making analyses of this material I have verified the existence of the new silicate here described. It is of an unusually simple composition for one of the rare earths.

The first analysis made gave the following results, which are the average of two closely agreeing determinations:—

Combined water	1.56
Alumina	0.15
Zirconia	71.88
Titanic acid	0.62
Ferrous oxide	0.43
Silica	25.31
	99.95

* Published by permission of the Director of the U.S. Geological Survey.

* Translated by J. C. Branner from the *Revista da Sociedade Brasileira de Ciencias*, No. 1, Rio de Janeiro, 1917, p. 31.

These results show that the material corresponds, in molecular composition, to a mixture of two or more compounds.

Taking into account the insolubility of zirconite ($ZrO_2 \cdot SiO_2$) the only silicate of zirconium thus far known by wet analysis, and verified by several determinations of materials that may be considered as absolutely pure, Derby suggested the possibility of making a separation of the component minerals in case they were different.

For this purpose a few grms. of the substance were treated for some hours with a mixture of hydrofluoric and hydrochloric acids. The only visible effect produced was an alteration of the colour of the fragments of the material, which changed from a dark grey to a yellowish white, but preserving perfectly their original angular appearance. The acid solution, however, showed with turmeric paper the characteristic reaction for zirconium, and the residue was easily broken up under slight pressure of a platinum spatula.

Filtering and washing in a funnel coated with Canada balsam, the dry residue was examined under a microscope ($\times 400$) and found to consist of microcrystalline aggregates radiating from centres and apparently homogeneous.

The homogeneity was confirmed by the analysis, and the residue had the exact composition of zirconite ($ZrO_2 \cdot SiO_2$). The quantity, however, which was 41 per cent of the original rock, corresponded to one-half of the silica contained in it.

It was evident that it was not a simple mixture of zirconite with an excess of zirconia (baddeleyite or brazilite), but two silicates, one of them insoluble in the humid reagents, and the other readily soluble. (Thin sections do not show the least sign of the presence of amorphous or crystalline silica).

At this point the investigation had to be suspended for some time to await the arrival of new material.

It is noteworthy that this first analytical work had suggested the following composition of the Caldas rock:—

Zirconite ($ZrO_2 \cdot SiO_2$)	41 (det.)
Silicate new? ($3ZrO_2 \cdot 2SiO_2$)	56
Impurities	3
	100

A second specimen had this composition—

Zirconia (ZrO_2)	85.01
Ferric oxide (Fe_2O_3)	3.57
Titanic acid (TiO_2)	1.52
Silica (SiO_2)	9.63
	99.73

Later, when the Geological Service had new material, Dr. Derby by using a needle and a microscope succeeded in separating a little more than 600 milligrams. of the visible homogeneous materials. Of this two parallel analyses were made which showed beyond question that the material was homogeneous, and that it was a new silicate with the following composition:—

Zirconia	68.04
Silica	25.45
Volatile matter and combined water	6.35
	99.72

Dividing these percentages by the molecular weights we have the molecular factors—

Zirconia	0.5565
Silica	0.4220
Water	0.3516

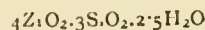
Dividing the molecular factors of the zirconia and of the water by the silica we have—

Zirconia	1.319
Silica	1.000
Water	0.833

Multiplying by three we have—

Zirconia	3.957
Silica	3.000
Water	2.499

Equal to—



or—



It seems possible that the high molecular weight and the consequent constitutional complexity corresponding to this formula may be responsible for the facility with which the mixture of hydrofluoric and hydrochloric acids attacks and dissolves it.

Inasmuch as the identification of this new mineral species was due entirely to the efforts and labours of Dr. Derby, I have the honour to propose for it the name of *Orvillite*.

II. Oliveiraitite.

My attention was called to the mineral euxenite in June, 1910, by a specimen given me for analysis by my colleague Jorge de Araujo Ferraz. There was very little of the material however. About a year later there was a discussion in one of our periodicals in regard to a new element derived from a mineral which, thanks to the studies of our learned Prof. Paes Leme of our museum, was shown to be not a new element, but an oxide of the rare earths composing the mineral euxenite.

In August, 1913, by order of Dr. O. A. Derby, then director of the Serviço Geológico, I had the pleasure of receiving a large number of specimens of this material from my colleague, who visited the place at which they occur on the fazenda Santa Clara, Tocantins station, on the Leopoldina railway in the municipality of Pomba, State of Minas Geraes. I made several analyses of the material, and the results were always in approximate agreement with those made at the Escola de Minas, and with one made at the Royal Polytechnic School at Turin and shown me by my colleague Ferraz. Thanks to the efforts of Prof. Paes Leme I obtained a small bit of material from an uncertain locality in Espírito Santo from which it was said the new element had been obtained.

In order to have a clear idea of the similarity of the materials from the two different places I give here the results of the analyses:—

Euxenite.

	Espírito Santo.	Pomba, Minas.
Tantallic acid	3.20	1.46
Columbic acid	28.70	36.39
Titanic acid	23.70	25.00
Oxide of cerium	—	0.46
Oxide yttrium (group)	23.12	23.08
Oxide zirconium	4.23	—
Oxide uranium	7.50	10.06
Oxide lead	0.14	0.14
Oxide tin (traces)	—	—
Oxide iron	3.12	—
Combined water	6.41	2.41
	100.12	99.00

At first, as is shown by the analysis of the euxenite from Pomba, the zirconia was not determined by me, but was included with the columbic acid.

Upon re-examining the material and also what the same collector brought in March, 1914, I verified the existence of a new mineral, a hydrated titanate of zirconium.

Having separated the mineral I submitted it to Dr. E. Rimmann, at that time the petrographer of the Geological Service, who made this note—

"It shows no distinct crystalline structure, but is amorphous; its colour in thin fragments is a yellowish green and shows in places multiple twinning and a fibro-radial structure approximating radio-spherulitic. Its optical characters correspond more or less with those produced in amorphous minerals in general by high pressure, a correspondence increased by the fact that the double refraction and the fibro-radial structure are strictly limited to the highly sheltered area of the mineral. Neither crystalline faces nor cleavage can be seen."

Where the mineral is entirely free from foreign bodies it is of a greenish yellow colour. A quantity of it separated under the microscope by Derby gave the following results when analysed:—

Zirconia, ZrO_2	63.36
Anhydrous titanitic acid, TiO_2	29.92
Combined water	6.48
	99.76

Dividing these percentages by the proper molecular weight we have—

Zirconia	0.517
Titanic acid	0.373
Water	0.360

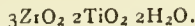
Dividing the molecular proportions by the zirconia we have—

Zirconia	1.000
Titanic acid	0.7215
Water	0.693

Multiplying by three we have—

Zirconia	3.00
Titanic Acid	2.16
Water	2.09

or—



I propose for this new mineral the name of *oliveiraite* in honour of the veteran geologist Dr. Francisco de Paula Oliveira, who has been so long associated with Dr. Orville Derby in the work upon the geology of this country. The presence of the oxide of zirconium in euxenite explains the origin of the new mineral as a secondary product of it.

Almost all of the crystals of euxenite are covered with a yellow crust that has the following approximate composition—

Columbic acid, Cb_2O_5	52.51
Including tantalitic acid, Ta_2O_5	
Titanic acid, TiO_2	25.00
Rare earths, R_2O_3	7.40
Oxide of uranium, UO_3 (a)	4.93
Combined water	11.14
	100.98

(a) On decomposition the uranium is present in the form of the oxide UO_3 , and in the unaltered mineral in the form of UO_2 .

It is clear that in the process of decomposition the euxenite has lost a part of the rare earths, oxide of uranium, and titanitic acid, but little or none of the earthy acids (Cb_2O_5 , Ta_2O_5).

Considering again the molecular relations of these two minerals, it is to be noted that in the relation between zirconia and silica in the first case, and between the zirconia and titanitic acid in the second, there is a small excess of acid in each.

In orvillite, for example, in place of the relation $4ZrO_2 \cdot 3SiO_2$ it is $3.96ZrO_2 \cdot 3SiO_2$.

In oliveiraite, in place of $3ZrO_2 \cdot 1TiO_2$, we have $3ZrO_2 \cdot 2.16TiO_2$.

This curious fact is notable in the minerals of zirconium. In Dana's great work there are given twelve analyses of zirconite, and in all of them the zirconia is low in relation to the silica, the mean being $ZrO_2 : SiO_2 = 1 : 1.024$ in place of $ZrO_2 : SiO_2 = 1 : 1$, or an excess of silica of 0.024 molecule for molecule.

In the case of orvillite this excess is 0.01 molecule for molecule, and in that of oliveiraite 0.08 molecule for molecule.—*American Journal of Science*, xlvii., No. 278.

THE GOVERNMENT AND THE ORGANISATION OF SCIENTIFIC RESEARCH.*

By SIR FRANK HEATH, K.C.B.,
Secretary, Department of Scientific and Industrial Research.

THE story that I have to tell this afternoon is the tale of a great adventure—one of the adventures of the great war. It was not undertaken as part of the campaign for victory in the field, but in order to help us to win the peace, a campaign now beginning and likely to be scarcely less difficult, though not as catastrophic, as the trials from which we have emerged. It was an adventure upon which the Government embarked in the summer of 1915, because, like all true adventures, it was an act of faith. The general direction of advance had been thought out, but the road was still to make and the result was as yet invisible. The problem the Government set itself was the encouragement and organisation of scientific research by direct State action. An experiment such as no country had ever attempted was undertaken by a people which, in some respects, is the most conservative in the world. We are not a nation with a finished theory of the functions and powers of government, and in that we are fortunate, for when the pressure of need arises we are willing to take courses which a more philosophical race would shun. Our enemies, whose political theory was worked out to the last detail, in confident contempt for the human nature with which it juggled, never dreamt of attempting the organisation of research by direct action of the State. They were more systematic, and, to do them justice, more zealous in their pursuit of science than any other nation. They could rely upon the effects of their highly organised State-regulated system of education. But had they found themselves in our shoes they would have discovered many excellent arguments to show the futility of attempting to organise research by State action. It would, indeed, have been an impossibility for the State as the Germans conceived it. Humboldt, in his famous unfinished memorandum to the Berlin Academy of Science, remarks: "The State must never forget that the achievement is not the State's nor ever can be; it must remember that whenever the State seeks to interfere, its action is always a hindrance; it must be content to realise that the work will proceed far better without it."

Humboldt was thinking of pure research—research, that is, in pure science and in learning of all kinds. It is clear, from all his remarks, that what we may call research in applied science for the purposes of industry and the practical convenience or well-being of life was not in his mind. But it is worth while, before I go on to explain what has been done by the Government in this country during the last few years, to say something in explanation both of what is meant by "research" throughout this paper and something about the research worker and his manner of work.

Research is a term which has been very much on our lips recently, and, as is usual in cases of this kind, it is by no means always used in one sense. The Patent Office speak of a research into the terms of previous patents, by which they mean making a search for already known and recorded facts; and the word is similarly used in many

* Read before the Royal Society of Arts, February 12, 1919.

cases where the sole activity is the seeking out, the collection, and collation of existing knowledge with a view to some definite course of action. Strictly speaking, this kind of work would be more properly described as a "search" rather than a "research." At any rate it is not the sort of work with which I am concerned this afternoon. Before research in its strict sense can begin it may be necessary to make a search for facts already known and recorded, but forgotten or overlooked. Such action is of the same preliminary kind as seeking for paper and ink and pens before beginning to write; but it is no more research in the strict scientific sense than the collection of pens, ink, and paper is authorship. In the meaning of the term as I am using it here research means the creation of new knowledge. It is an actual extension of the powers and capacity of man in relation to the world in which he lives, and the extension which comes from the systematic work of the original mind upon material already to hand often takes place in a direction quite different from that which is anticipated when the worker begins his labours. That is the reason for comparing research to "the wind which bloweth whither it listeth." Discoverers, in describing the history of important discoveries, have told us over and over again of this fact—a fact so frequent and pronounced that in some cases it may almost be said that a worker has blundered upon a new truth. It is not extraordinary, because the excursions of the researcher are always into a new and unmaped country, and no man can tell until he reaches it what the lie of the land is. The more concrete the field of science the more true will this be found to be. It is not surprising, in these circumstances, that the researcher himself should plead for freedom, and maintain, indeed, that without it his usefulness is lost. That is the central idea of Humboldt's thesis. That is why, in his view, the State must do damage by interference, and, indeed, if the State interlopes with the natural processes of research work it *can* only do harm. In a sense the true research worker is an anarchist. He can recognise no laws of procedure but those of his own science and of his own method of attack. These are severe enough, and they can tolerate no external action which seeks to place him in blinkers and to force him to run at the discretion of men who cannot see with his eyes. The great question that is to be solved is whether it is possible, under these conditions, for the State to take action which will stimulate research without interfering with it when we mean by "research" nothing but the creation of new knowledge; and whether, in the application of new knowledge to specific problems which the State in one or other of its capacities seeks to have solved, it can do anything effective towards the organisation of the attack upon these problems. This second type of research does not call for the same degree of originality as the creation of new knowledge; but on the one hand it cannot proceed without the assistance of pure research, and on the other it is constantly revealing gaps in human knowledge which call for investigation by the pure researcher. Moreover, though much of the work in applied science is less fundamental in character, it is also, because of the large number of factors which are involved, far more complicated, and it calls for team work among researchers in an ever-growing degree. But you cannot have team work without organisation. To repeat my question again: Is it possible for the State, on the one hand, to *encourage* pure research, and on the other hand to *organise* applied research?

This, then, was the adventure. I need not spend time here in explaining why something had to be done. You know the difficulties with which we were faced. Important raw materials under enemy control, semi-manufactured products of vital importance made only by them, finished articles essential to our staple industries or to our fighting services drawn almost entirely from enemy sources—you know the list, and you know something of the brilliant efforts made in our emergency to supply what was missing. We have submitted to State action with a vengeance. But the Government realised that emergency

measures could not offer a lasting cure for our shortcomings. An attempt must be made to organise for peace. What did they do? The traditional way of dealing with a problem of this kind is to appoint a Royal Commission of distinguished persons to study the question and recommend the action to be taken. But wise men can seldom agree to appear before the public with exactly the same answers to a question, and if the wise men disagree it becomes harder than ever to decide what should be done. Besides, time will have passed, and the problem may not seem any longer so urgent, because other problems have arisen which are clamouring for solution. Moreover, the wise men are not made responsible for carrying their advice into effect. Before anything can be done they have disappeared from the scene, and this little omission encourages argument and theory. So the Government appointed a Commission to act as permanent advisers to a responsible Minister. The Minister selected was the Lord President of the Council, because it was realised that if research was to be organised effectively, it must cover not only the whole United Kingdom, but be able to co-operate easily with possible developments of a like kind in other parts of the Empire. It was also clear that if the Government was to obtain the co-operation of the industries in regard to research, the department concerned should be free from any suspicion of being concerned either in their regulation or in commercial dealings with them. The Minister responsible should accordingly be unconnected with any administrative department of State. These considerations led naturally to the selection of the Lord President, for the Privy Council is the only department which has relations with the whole Empire, and which is free from administrative responsibilities. Parliament voted the minister, or rather a Committee of the Privy Council of which he was chairman, a sum of money to spend on the encouragement and organisation of scientific research—not a fixed sum, but an annual vote susceptible of increase. By an Order in Council, all proposals for spending money upon these purposes stand referred to the permanent commission which is called the Advisory Council for Scientific and Industrial Research. And the Advisory Council can initiate proposals of their own. It was a small but most significant change in the traditional procedure. The idea of making the Commission permanent was not new. There have been a good many permanent advisory committees to Government departments. The provision for changing the *personnel* from time to time is not new. The selection of a small body of men specially qualified to deal with the subject in hand is not new. The novel feature was the delegation of the responsibility for thinking out a policy to a permanent body of experts who are not civil servants, and making this expert body an integral part of the machine by giving them the services of the permanent staff of the department, and keeping them continually informed of every departmental procedure. This was ensured by providing them with an administrative chairman who has devoted his whole time to the work, and with a secretariat which includes the heads (instead of the junior members) of the administrative staff. In a word, the Minister, instead of relying upon his officials for advice (whether technical or administrative), supplemented by such occasional guidance upon particular questions as he might refer to temporary Royal Commissions or to permanent Advisory Committees, placed all his technical advice in commission, and entrusted it to a body of seven independent and distinguished men of science, the majority of whom were also large industrialists. The result of this experiment has been most interesting. The general policy of the Minister and of the Government has been worked out, not by the official, but by the Advisory Council. The Council has watched the effects of the action it has recommended and has gradually built up a method of procedure consonant with the original intention of the Government. Stated in its simplest terms, the intention of the Government in the Order in Council of

July 28th, 1915, was to delegate to independent experts the duty of devising the methods by which scientific and industrial research should be encouraged and developed. The Advisory Council, as we shall see, have carried this principle through in all the proposals which they have made. The Government had reached the conclusion, before they issued the Order in Council establishing the new organisation, that action was needed in three main directions. In the first place research was needed in a number of directions hitherto neglected; secondly, it would be necessary to establish new institutions or to develop existing institutions for the scientific study of problems affecting particular industries and trades. And finally it was clear that the number of trained research workers in the country was inadequate to our needs. The information possessed by the Board of Education was clear on this point, and had led the President, Mr. Joseph Pease (now Lord Gainford), to urge the establishment of the new organisation which your Lordship later set up as an independent department. All these three main lines of action were mentioned in the original Order in Council, and proposals in regard to them stood referred to the Advisory Council. How did the Council proceed? They began as an interim measure by recommending the Minister to assist a number of researches conducted by scientific and professional societies which were languishing as a result of the war, and they also recommended grants to the National Physical Laboratory for an urgent research into the methods of manufacturing optical glass, and to a committee at the Central School of Pottery at Stoke-on-Trent for research into the manufacture of hard porcelain from British materials. This research has had most successful and promising results. Meantime the Council have gradually and steadily worked out, in consultation with university professors and teachers in technical schools, with the leaders in many of our principal industries, and with each of the Government Departments, a systematic procedure along the whole front, which has not only commended itself to the responsible Minister and to the Government of the day, but has been adopted or is being adopted by each of the self-governing Dominions with variations suited to local conditions, and by three at least of our Allies (America, France, and Japan).

I will divide the field of work into the three main divisions already indicated and will deal with them, for convenience, in the following order: (i.) The encouragement of research workers; (ii.) The organisation of research by industries, and (iii.) The organisation of national research.

In dealing with each of these matters, the policy advocated by the Advisory Council and adopted by the Minister has been that laid down by the Government when the Department was founded, viz., the delegation of responsibility for each kind of service to the expert within the limits imposed by the ultimate responsibility of the Minister to Parliament, and of the Accounting Officer to the Controller and Auditor General.

(To be continued).

MELTING-POINTS OF CHEMICAL ELEMENTS AND OTHER STANDARD TEMPERATURES.

REVISED, JULY 15, 1918.

This table of melting-points of the chemical elements is issued in answer to numerous requests for this information.

The values of the melting-points used by the Bureau of Standards as standard temperatures for the calibration of thermometers and pyrometers are indicated in capitals. The other values have been assigned after a careful survey of all the available data.

As nearly as may be, all values, in particular the standard points, have been reduced to a common scale, the thermodynamic scale. For high temperatures, and for use with optical pyrometers, this scale is satisfied very

exactly by taking $c_2 = 14,350$ in the formula for Wien's law (U.S. Bureau of Standards Circular No. 7, or *Scientific Paper No. 11*) connecting λ , monochromatic luminous intensity of wave-length λ , and T , absolute temperature:—

$I_\lambda = c_1 \lambda^{-5} e^{-\frac{c_2}{\lambda T}}$. For all purposes, except the most accurate investigations, the thermodynamic scale is identical with any of the gas scales.

At high temperatures some of the values are quite uncertain; thus, while the melting-point of platinum may be considered accurately known to 10°C. , that of tungsten is possibly uncertain by 50°C. or more. Temperatures centigrade are rounded off, and the exact Fahrenheit equivalents are usually given.

Melting-points of the Chemical Elements.

Element.	C.	F.
Helium	< -271	< -456
Hydrogen	-259	-434
Neon	-253 ?	-423
Fluorine	-223	-369
Oxygen	-218	-360
Nitrogen	-210	-346
Argon	-188	-306
Krypton	-169	-272
Xenon	-140	-220
Chlorine	-101.5	-150.7
MERCURY	-38.87	-37.97
Bromine	-7.3	+18.9
Cæsium	+26	79
Gallium	30	86
Rubidium	38	100
Phosphorus	44	111
Potassium	62.3	144.1
Sodium	97.5	207.5
Iodine	113.5	236.3
Sulphur	S _I 112.8	235.0
	S _{II} 119.2	246.6
	S _{III} 106.8	224.2
Indium	155	311
Lithium	186	367
Selenium	217—220	423—428
TIN	231.9	449.4
Bismuth	271	520
Thallium	302	576
CADMIUM	320.9	609.6
LEAD	327.4	621.3
ZINC	419.4	786.9
Tellurium	452	846
ANTIMONY	630.0	1166.0
Cerium	640	1184
Magnesium	651	1204
ALUMINIUM	658.7	1217.7
Radium	700	1292
Calcium	810	1490
Lanthanum	810 ?	1490
Strontium	> Ca < Ba ?	—
Neodymium	840 ?	1544
Arsenic	850	1562
Barium	850	1562
Praseodymium	940	1724
Germanium	958	1756
SILVER	960.5	1760.9
GOLD	1063.0	1945.5
COPPER	1083.0	1981.4
Manganese	1230	2246
Beryllium (glucinum)	1280	2336
Samarium	1300—1400	2370—2550
Scandium	?	—
Silicon	1420	2588
NICKEL	1452	2646
Cobalt	1480	2696
Yttrium	1490	2714
IRON	1530	2786
PALLADIUM	1549	2820
Chromium	1615	2939

Melting points of Chemical Elements (continued).

Element.	C.	F.
Zirconium	1700 ?	3090
Columbium (niobium)	1700 ?	3090
Thorium	>1700	>3090
Vanadium	<Mo	—
PLATINUM	1720	3128
Ytterbium	1755	3191
Titanium	?	—
Uranium	1800	3272
Rhodium	<1850	<3360
Boron	1950	3542
Iridium	2200—2500 ?	4000—4500
Ruthenium	2350 ?	4260
Molybdenum	2450 ?	4440
Osmium	2550	4620
Tantalum	2700 ?	4890
TUNGSTEN	2900	5250
Carbon	3400	6152
	>3600	>6500

Other Standard Temperatures.

Substance.	Phenomenon	C.	F.
Oxygen	Boiling	-183.0	-297.4 (a)
Carbon dioxide	Sublimation	-78.5	-109.3 (b)
Sodium sulphate, $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$	Transformation into anhydrous salt	32.384	90.291
Water	Boiling	100	212 (c)
Naphthalene	"	217.96	424.33 (d)
Benzophenone	"	305.9	582.6 (e)
Sulphur	"	444.6	832.3 (f)
$3\text{Ag}_2\text{Cu}$	Eutectic freezing	779	1434
Sodium chloride	Freezing	801	1474

Variation with pressure (pressure in mm. of Hg).

- (a) $C^\circ = -183.0 + 0.01258 (p - 760) - 0.0000079 (p - 760)^2$.
 (b) $C^\circ = -78.5 + 0.01595 (p - 760) - 0.0000111 (p - 760)^2$.
 (c) $C^\circ = 100 + 0.03670 (p - 760) - 0.00002046 (p - 760)^2$.
 (d) $C^\circ = 217.96 + 0.058 (p - 760)$.
 (e) $C^\circ = 305.9 + 0.063 (p - 760)$.
 (f) $C^\circ = 444.6 + 0.0908 (p - 760) - 0.000047 (p - 760)^2$.

—U.S. Bureau of Standards Circular No. 35, 3rd Edition.

ORDERS OF THE MINISTRY OF MUNITIONS.

CONVERTER PLANT.

In reference to the Converter Plant Control Order, 1918, dated April 5, 1918, the Minister of Munitions hereby orders as follows:—

1. The operation of the said Order is hereby suspended on and after the date hereof (March 4) until further notice.
2. Such suspension shall not affect the previous operation of the said Order or the validity of any action taken thereunder, or the liability to any penalty or punishment in respect of any contravention or failure to comply with the said Order prior to such suspension, or any proceedings or remedy in respect of any such penalty or punishment.
3. This Order may be cited as the Converter Plant Control (Suspension) Order, 1919.

ROSIN AND ROSIN OIL.

In reference to the Rosin Control Order, 1918, dated January 31, 1918, the Minister of Munitions hereby orders as follows:—

1. The operation of the said Order is hereby suspended on and after May 1, 1919, until further notice.
2. Such suspension shall not affect the previous operation of the said Order or the validity of any action taken thereunder, or the liability to any penalty or punishment in respect of any contravention or failure to comply with the said Order prior to such suspension, or any proceeding or remedy in respect of such penalty or punishment.
3. This Order may be cited as the Rosin Control (Suspension) Order, 1919.

THE GOVERNMENT SCHEME FOR INDUSTRIAL RESEARCH.

THE Government have placed a fund of a million sterling at the disposal of the Research Department to enable it to encourage the industries to undertake research, and the Advisory Council for Scientific and Industrial Research have recommended, after consultation with manufacturers and others, that this new fund should be expended on a co-operative basis in the form of liberal contributions by the Department towards the income raised by voluntary associations of manufacturers established for the purpose of research. By this method the systematic development of research and the co-operation of science with industry will be carried out under the direct control of the industries themselves. The fund for each industry will be expended by a Committee or Board appointed by the contributing firms in the industry, and the results obtained will be available for the benefit of the contributing firms.

It is anticipated that each firm subscribing to a research organisation will have the following privileges:—

- (i) It will have the right to put technical questions and to have them answered as fully as possible within the scope of the research organisation and its allied associations.
- (ii) It will have the right to recommend specific subjects for research, and if the Committee or Board of the research organisation of that industry consider the recommendation of sufficient general interest and importance, the research will be carried out without further cost to the firm making the recommendation, and the results will be available to all the firms in the organisation.
- (iii) It will have the right to the use of any patents or secret processes resulting from all researches undertaken without payment for licences, or at any rate on only nominal payment as compared with firms outside the organisation.
- (iv) It will have the right to ask for a specific piece of research to be undertaken for its sole benefit at cost price, and, if the Governing Committee or Board approve, the research will be undertaken.

No firm outside the organisation will have any of these rights. It will often be advisable for a Research Association to set up a Bureau of Information which will give to each of its members technical information relating to the industry. If this is done each firm will have the following privileges:—

- (i) It will receive a regular service of summarised technical information which will keep it abreast of the technical developments in the industry at home and abroad.
- (ii) It will be able to obtain a translated copy of any foreign article in which it may be specially interested and to which its attention will have been drawn by the periodical bulletin.

The method of assessing the subscription of each firm will have to be determined in negotiation with each industry or section of an industry which may agree to combine for the purposes of research, but the intention is that firms should contribute on a basis proportionate to their size.

The Department is advised that the best machinery for the purpose in view is the establishment of Research companies limited by guarantee of a nominal sum, e.g., £1 and working without profit, i.e., without the division of profits among the members in the form of dividends. Any such Association will be qualified to apply for grants towards its income from the Research Department under stated conditions, and when necessary a Government grant will be given for a period of years to be agreed upon. The whole of the results of researches conducted by any Research Association will belong to the Association itself, which will hold them in trust for the benefit of its members, but the Government will keep in its own hands two powers—the right of veto in case any proposal is

made by a Research Association to communicate any results of research to a foreign person, or to a foreign corporation, and the right, after consultation with the Association concerned, of communicating the results of discoveries to other industries for their use on suitable terms. The Department will not, however, make any results obtained by a Research Association available to firms or individuals who are eligible for membership of that Association but have not joined it.

Thus the policy of the Research Department is to delegate the prosecution of industrial research on a co-operative basis to the industries themselves, working through voluntary associations of firms engaged in producing similar articles or using the same materials. It is hoped and anticipated that these Associations will co-operate with each other in the solution of problems of common interest, and the Department intends to do its utmost to encourage such alliances. It is also anticipated that the Associations will make every possible use of existing facilities for scientific research whether at the Universities and Technical Colleges, or at such central institutions as the National Physical Laboratory. There will be ample scope for all these agencies as well as for any special research institutes which the Research Associations may establish in future for their own purposes.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, February 27, 1919.

Sir J. J. THOMSON, President, in the Chair.

The following papers were read:—

"Scattering of Light by Solid Substances." By Hon. R. J. STRUTT, F.R.S.

Glasses of all kinds show a strong internal scattering of light. The beam viewed laterally is strongly, but not completely, polarised. Yellow and smoky quartz also show a strong scattering. One specimen gave a polarisation so nearly complete that an analysis set for minimum intensity transmitted only 0.7 of 1 per cent of the scattered light.

If a polarised beam is passed along the axis of such a quartz crystal, there are for a given wave-length maxima and minima of scattered light along the length of the beam. This is due to the rotatory property. Owing to rotatory dispersion the period is different for different wave-lengths, and coloured bands result.

The clearest and whitest quartz has some scattering power, though much less than that of glass or liquids. In one case examined the intensity was about eight times that due to dust-free air at atmospheric pressure.

This small scattering is considered to be due to inclusions, as in the case of visibly smoky or yellow quartz. The regular atomic structure, which has a period small compared with the wave-length of ordinary light, should give no scattering. For very short wave-lengths (X-rays) the well-known diffraction effects of crystals come in.

"Constitution of Sulphur Vapour." By Sir JAMES DOBBIE, F.R.S., and J. J. FOX, D.Sc.

Investigations based on the determination of the vapour density leave the question of the existence of sulphur molecules intermediate in complexity between S_8 and S_2 unsettled. The present paper contains an account of an attempt to solve the problem by the study of the absorptive power of the vapour of sulphur for light under various conditions of temperature. When light from a suitable source is passed through the vapour and examined with the spectroscopic at successively higher temperatures it is found that the amount of absorption caused by the vapour gradually increases up to about 650°C .

after which it decreases as the temperature rises until 900°C . is reached, above which no further change occurs.

The changes in absorptive power cannot be explained on the view that the more complex molecules which exist near the boiling-point gradually break down into diatomic molecules without the formation of molecules of intermediate complexity, for in that case the change of absorption would proceed regularly in one direction with rise of temperature. The fact that it first increases to a maximum at 650°C . and then decreases points to the existence at that temperature of molecules more highly absorbent than either the octatomic or the diatomic molecules.

The density of sulphur vapour at 650°C . corresponds closely with the molecular formula S_3 . It seems probable, therefore, that the highly absorbent sulphur molecules existing at that temperature have a constitution analogous to that of ozone, and it is noteworthy in this connection that the absorptive power of ozone is very much greater than that of ordinary oxygen.

"Pressure upon the Poles of the Electric Arc." By W. G. DUFFIELD, D.Sc., T. H. BURNHAM, and A. H. DAVIS.

For many reasons the projection of electrons from the cathode of an electric arc is to be expected, and the mechanism of the arc appears to require it. If this projection exists it is likely to occasion a mechanical recoil upon the cathode. A pressure was looked for in 1912 and discovered. It remained to determine if the magnitude was such as to be accounted for by electronic projection. Numerous sets of observations upon anode and cathode were taken with varying current and arc length and different dispositions of apparatus. This generally consisted of an arm suspended by a torsion fibre and having a carbon pole fixed at right angles at one end, the arc being formed between this and a fixed carbon rod. Corrections were made for the torque due to the magnetic field of the earth and the rest of the circuit, and the outstanding pressure found to be about 0.17 dyne per ampere, or when convection current effects were eliminated as far as possible, 0.22 dyne per ampere.

The effect does not appear to be due to radiometer action, and is about 200 times too small to be referred to the expulsion of carbon atoms at the boiling-point of that element. The ratio e/m may be calculated, since $2P = mnv$, where P is the observed pressure over a hemispherical pole and n the number of carriers leaving the pole per second with velocity v ; further the current $c = ne$, and if the potential drop across the pole face is V ,

we have $Ve = \frac{1}{2} mv^2$. It follows that—

$$e/m = \frac{1}{2} V \left(\frac{C}{P} \right)^2 \text{ and } v = V \left(\frac{C}{P} \right).$$

Using Duddell's datum for V we find $e/m = 6.4 \times 10^7$ and $v = 2.8 \times 10^8$ cm./sec. Making additional assumptions, of which the chief is that half the current is atom borne, $e/m = 1.6 \times 10^7$ and $v = 1.4 \times 10^8$ cm./sec. Such evidence as has been obtained thus favours the recoil being due to the projection of electrons. This conclusion is stated with some reserve, but there can be no doubt as to the existence of the pressure. The paper discusses the relation between this phenomenon and photoelectric and thermionic effects and the production of polar lines in arc spectra of metals.

Royal Institution.—Next Tuesday, March 18, at 3 o'clock, Prof. A. Keith will deliver the first of a course of four lectures at the Royal Institution on "British Ethnology—the People of Scotland." On Thursday, March 20, Prof. C. H. Lees will give the first of two lectures on "Fire Cracks and the Forces Producing them." The Friday discourse on March 21, at 5.30, will be delivered by Prof. W. W. Watts on "Fossil Landscapes"; on March 28 the Right Hon. Sir J. H. A. Macdonald on "The Air Road."

NOTICES OF BOOKS.

Petroleum Refining. By ANDREW CAMPBELL. London: Charles Griffin and Co., Ltd. 1918. Pp. xv+297. Price 25s. net.

UP to the present there has been no book in the English language devoted exclusively to the subject of petroleum refining, but this gap in our literature is now well filled by this very useful treatise, in which the ordinary methods of treatment, not including "cracking," are excellently described. The examination of the crude oil is first discussed in perhaps rather unnecessary detail; for example, there ought to be no need to explain to the technologist how to convert temperatures from the Fahrenheit to the Centigrade scale. Full directions are given for the performance of flash-point determinations, and an extensive account is provided of the Lovibond tintometer and its use in colour determination. The second chapter is devoted to a description of the equivalent and arrangement of the refinery, and then the methods employed are discussed in turn, many diagrams and plans being provided as well as illustrations, sometimes not specially instructive, of machinery and plant. A short account is given of candle-making. Detailed engineering specifications are provided, and a particularly full list of references to the literature of petroleum refining, in which all articles, &c., in the English language, which are likely to be useful to the refiner, are included.

BOOKS RECEIVED.

"Osmotic Pressure." By ALEXANDER FINDLAY, M.A., D.Sc., F.I.C. Second Edition. London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. 1919. Pp. xi+116. Price 6s. net.

"Chimica delle Sostanze Esplosive." By MICHELE GIUA. Milan: Ulrico Hoepli. 1919. Pp. xvi+556. Price L.28.

MISCELLANEOUS.

Motor Owners Further Action.—The National Council of the Commercial Motor Users Association (Incorporated) has been informed that the Government will shortly require employers to join a suitable Federation in order to regularise dealings with Labour. The Council has accordingly entered into an arrangement with the Motor Transport Employers Federation under which the new conditions can be met by haulage contractors and other owners of commercial motor wagons or vans. Captain F. G. Bristow, who is Secretary to the two bodies, can be addressed at 83, Pall Mall, London, S.W.1, for fuller information.

MEETINGS FOR THE WEEK.

- MONDAY, 17th.—Royal Society of Arts, 4.30. (Cantor Lectures). "Coal and its Conservation," by Prof. W. A. Bone.
- TUESDAY, 18th.—Royal Institution, 3. "British Ethnology—The People of Scotland," by Prof. A. Keith.
- Institution of Petroleum Technologists, 5.30. "Plant Employed in the Percussion Systems of Drilling Oil Wells," by M. A. Ockendeo and A. Carter.
- WEDNESDAY, 19th.—Royal Society of Arts, 4.30. "Distribution of Heat, Light, and Motive Power by Gas and Electricity," by S. R. Dugald Clerk.
- THURSDAY, 20th.—Royal Institution, 3. "Fire Cracks and the Forces producing them," by Prof. C. H. Lees.
- Chemical Society, 8. "Rotatory Dispersive Power of Organic Compounds—Part IX., Simple Rotatory Dispersion in the Terpene Series," by T. M. Lowry and H. H. Abram.
- FRIDAY, 21st.—Royal Institution, 5.30. "Fossil Landscapes," by Prof. W. W. Watts.
- SATURDAY, 22nd.—Royal Institution, 3. "Spectrum Analysis and its Application to Atomic Structure," by Prof. Sir J. J. Thomson, O.M.

Assistant Analyst (Woman), four years' experience in General Analytical Laboratory (Foods, Brewing-sugars and Malts, Chemicals, &c.), desires London permanency. Matriculated with Chemistry. Salary £150.—Address, V. A. H., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Assistant, aged 21 to 24 years, required in Analyst's Laboratory.—Write, giving particulars of experience, &c., to O. A., care of Street's, 30, Cornhill, E.C. 3.

Chemist, aged 24, seeks permanent Position in Laboratory in or near London. Seven years' experience in analysis of Oils, Fats, Waxes, Soaps, Glycerin. Knowledge of French.—Address, "C. 24," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Demobilised Cadet (19) requires Situation in Laboratory. Good all round education; Public School. Passed Inter. B.Sc. One year's previous experience.—Address, J. C. H., 23, Westcott Street, Hull.

French Young Man, aged 20 (French Baccalaureate Sc. Phil.), requires Employment in Chemical Works or Laboratory.—Address, J. M. Lerpette, 22, Rue des Guetteries, Tours (T. ea L.), France.

The Council of the INSTITUTE OF CHEMISTRY are proceeding to the appointment of an ASSISTANT SECRETARY, at an initial salary of £450 per annum. —Candidates, who must be Members of the Institute, are invited to communicate at once with the REGISTRAR, Institute of Chemistry, 30, Russell Square, London, W.C. 1.

Works Analytical Chemist required. One conversant with Soap Manufacture, Nicotine Extractions, and Agricultural and Horticultural Preparations. State full particulars and salary required.—Address, W. A., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Experienced Research Chemist and Analyst, with excellent Laboratory facilities in City, is now free to undertake RESEARCHES connected with the manufacture of CHEMICALS, INTERMEDIATES, DYES, &c.; also the Utilisation of WASTE PRODUCTS and all classes of ANALYSIS.—"Laboratory," 7, 8, & 9, Bolt Court, Fleet Street, London.

SWANSEA TECHNICAL COLLEGE.

Wanted, a STEWARD for the CHEMICAL LABORATORY. Good wages to a competent man. Apply in writing, stating experience, to the PRINCIPAL.

Education Offices, Swansea.

T. J. REES.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—A. P. LAURIE, M.A., D.Sc.

SPECIAL FIRST, SECOND, and THIRD YEAR INTENSIVE COURSES for Students demobilised from the Forces will commence on APRIL 15 next and continue till JULY 25, in the subjects of—

MECHANICAL ENGINEERING,
ELECTRICAL ENGINEERING,
MINING ENGINEERING.

These Courses will be suitable for Students desiring to refresh their knowledge, or who wish to qualify for the Diploma of the College, and will count as equivalent to one year of the usual Three Years' Course for the Diploma, either in the First, Second, or Third Years. Fee, £12 12s.; Matriculation Fee, 5s.

APPLIED CHEMISTRY.

Similar Courses in Applied Chemistry can also be obtained.

The attention of Demobilised Students is directed to the arrangements made by the Government for Payment of Fees and Maintenance of approved applicants.

Students desiring to enrol must apply, stating full particulars as to their pre-war University or Technical College training to the Interim Principal.

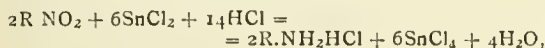
THE CHEMICAL NEWS

VOL. CXVIII., No. 3075.

THE ESTIMATION OF NITRO-GROUPS IN ORGANIC COMPOUNDS BY MEANS OF STANNOUS CHLORIDE.

By J. G. F. DRUCE, B.Sc.

MANY nitro-compounds can be reduced to the corresponding amino-compounds by means of stannous chloride in the presence of hydrochloric acid. This reaction, which may be expressed by the general equation—



is found to be nearly always quantitative, and thus constitutes a method for the exact determination of the percentage of nitro-group in an organic compound.

Altmann (*Fourn. Prakt. Chem.*, 1901, clxii., 370) has tested the trustworthiness with a number of various types of nitro-derivatives in the following simple way. A weighed quantity of the nitro-compound was added to a known volume of stannous chloride solution, the strength of which was known. After warming, the solution was made up to a known volume and an aliquot part was titrated with a decinormal solution of iodine, or when the solution was deeply coloured, with a decinormal potassium permanganate solution.

In an earlier paper by S. W. Young (*Fourn. Am. Chem. Soc.*, 1897, xix., 812) an account is given of a more elaborate method which was used in the case of *m*-dinitrobenzene. This method, with slight modifications, has now been tried for a number of nitro-compounds and is found to give very satisfactory results. The procedure adopted in the present work was as follows:—A weighed quantity (about 0.2 to 0.6 gm.) of the nitro-compound was placed in an Erlenmeyer flask of 200 cc. capacity and about 30 cc. of alcohol were added. The flask was connected to a Kipp's apparatus, which generated carbon dioxide. A slow stream of the gas was passed into the flask whilst it was warmed on a water-bath. When the carbon dioxide had displaced the air in the flask, 50 cc. of the stannous chloride solution of known strength were added. The mixture was then warmed for two hours on the water-bath, a slow stream of carbon dioxide being passed through all the time. The flask was then allowed to cool, and when cold was disconnected and titrated with a decinormal solution of iodine, starch being used as indicator.

The stannous chloride solution used was prepared by dissolving 25 grms. of tin in 250 cc. of concentrated hydrochloric acid and then making up the solution to 1000 cc. It was standardised against the iodine solution immediately before use in each case as it gradually oxidised.

EXPERIMENTAL.

Nitrobenzene.

1. 0.3747 gm. was dissolved in 30 cc. of alcohol; 50 cc. of stannous chloride solution were added. The excess of the latter required 20.75 cc. of the decinormal iodine solution. Originally 10 cc. of the stannous chloride solution required 40.50 cc. of iodine solution.

Volume of stannous chloride oxidised by the iodine solution—

$$= \frac{20.75 \times 10}{40.50} \text{ cc.} = 5.12 \text{ cc.}$$

Volume of stannous chloride oxidised by the nitro-group—

$$= 50.00 - 5.12 \text{ cc.} = 44.88 \text{ cc.}$$

Percentage NO_2 —

$$= \frac{44.88 \times 0.405}{1000} \times \frac{46}{6} \times \frac{100}{0.3747} = 37.20 \text{ per cent.}$$

2. 0.3532 gm. was dissolved in alcohol; 50 cc. of stannous chloride solution were added. The excess required 31.40 cc. of the iodine solution. Percentage $NO_2 = 37.26$.

3. 0.3380 gm. was dissolved in alcohol; 50 cc. of stannous chloride solution were added. The excess took 38.65 cc. of iodine solution. Percentage $NO_2 = 37.17$. $C_6H_5NO_2$ requires 37.39 per cent NO_2 .

o-Nitrotoluene.

1. 0.3838 gm. was dissolved in alcohol; 50 cc. of stannous chloride solution were added. The excess required 32.2 cc. of the iodine solution. Percentage $NO_2 = 34.02$.

2. 0.3528 gm. was dissolved in alcohol; 50 cc. of stannous chloride solution were added. The excess required 46.40 cc. of iodine solution. Percentage $NO_2 = 33.94$. $C_7H_7NO_2$ requires 34.37 per cent NO_2 .

m-Nitroaniline.

1. 0.4012 gm. was dissolved in alcohol; 50 cc. of stannous chloride solution were added. The excess needed 28.80 cc. of iodine solution. Percentage $NO_2 = 33.21$.

2. 0.3528 gm. was dissolved in alcohol; 50 cc. of stannous chloride solution were added. The excess required 49.5 cc. of iodine solution. Percentage $NO_2 = 33.29$.

3. 0.3613 gm. was dissolved in alcohol; 50 cc. of stannous chloride solution were added. The excess took 45.6 cc. of iodine solution. Percentage $NO_2 = 33.31$. $NH_2 \cdot C_6H_4 \cdot NO_2$ requires 33.25 per cent NO_2 .

p-Nitroaniline.

1. 0.4052 gm. was dissolved in alcohol; 50 cc. of stannous chloride solution were added. The excess needed 27.75 cc. of iodine solution. Percentage $NO_2 = 33.08$.

2. 0.3593 gm. was dissolved in alcohol; 50 cc. of stannous chloride solution were added. The excess needed 45.30 cc. of iodine solution.

10 cc. of stannous chloride was here (and subsequently) equivalent to 40.10 cc. of the iodine solution. Percentage $NO_2 = 33.12$. $NH_2 \cdot C_6H_4 \cdot NO_2$ requires $NO_2 = 33.25$ per cent.

m-Dinitrobenzene.

1. 0.2558 gm. was dissolved in alcohol; 50 cc. of stannous chloride solution were added. The excess took 18.65 cc. of iodine solution. Percentage $NO_2 = 54.51$.

2. 0.2308 gm. was dissolved in alcohol; 50 cc. of stannous chloride solution were added. The excess needed 36.50 cc. of iodine solution. Percentage $NO_2 = 54.47$.

3. 0.2614 gm. was dissolved in alcohol; 50 cc. of stannous chloride solution were added. The excess required 14.05 cc. of iodine solution. Percentage $NO_2 = 51.70$. $C_6H_4(NO_2)_2$ requires $NO_2 = 54.76$ per cent.

p-Nitrophenol.

1. 0.3385 gm. was dissolved in alcohol; 50 cc. of stannous chloride solution were added. The excess required 54.5 cc. of iodine solution. Percentage $NO_2 = 33.06$.

2. 0.3783 gm. was dissolved in alcohol; 50 cc. of stannous chloride solution were added. The excess required 37.95 cc. of iodine solution. Percentage $NO_2 = 32.89$. $HO \cdot C_6H_4 \cdot NO_2$ requires $NO_2 = 33.08$ per cent.

THE GOVERNMENT AND THE ORGANISATION
OF SCIENTIFIC RESEARCH.*By SH F. ANK HEATH, K.C.B.,
Secretary, Department of Scientific and Industrial Research.

(Concluded from p. 129).

THE ENCOURAGEMENT OF RESEARCH WORKERS.

THE Advisory Council confirmed at an early stage the fears of a shortage in the numbers of trained research workers. The Consultative Committee of the Board of Education had reported in 1916 on the need for enlarging the output of our universities, and more recently the Prime Minister's Committee on the Teaching of Science, under the chairmanship of the President of the Royal Society, has urged "that a large increase in the number of students passing through our universities is a matter of great national importance." The large plans recommended by the Advisory Council for the extension of research work will increase the demand for trained workers already inadequate for existing needs. The Research Department cannot directly ensure a larger entry to the universities and technical colleges, or assist young men and women during their undergraduate period, but it has already done something to help those who have acquired enough knowledge to begin research or who have shown capacity for original investigation. During the academic year 1916-17, a sum of over £3500 was spent in this way, in spite of the continued withdrawal of young men for military service. In 1917-18 the expenditure rose to £7500 and during the current year to £10 000. Now that men are returning in large numbers from the fighting services to the colleges and universities it is anticipated that over £30,000 can usefully be expended on this service during next academic year. The method of procedure adopted by the Advisory Council is as follows: In the first place, there are no scholarships or fellowships. The grants are not honorific awards carrying titles and encouraging the competitive instinct. The amount of the grant is determined within wide limits by the circumstances of each individual case. In the next place the applications are made upon the personal responsibility of the head of the department in the institution to which the worker is attached; or, if the applicant is a private worker, upon the personal responsibility of a man of scientific standing who vouches for the case and speaks as to the circumstances. Careful records are kept of the performances of workers recommended by professors and others, and the value of their recommendations is assessed accordingly. It has been found that this delegation of responsibility has worked well, much better indeed than the practice of leaving recommendations to boards of studies or to the university in its corporate capacity. And naturally so, for no one knows a student or worker so well as the man with whom he has worked. Each application comes before a Committee of the Advisory Council, and they make the award after consultation in particular cases with carefully chosen referees outside the Department. The grants made are of four kinds: (i.) Maintenance grants to students to enable them to be trained in methods of research; these grants are made for a year, but may be renewed for a second year. (ii.) Grants to independent research workers devoting their whole time to research, whether in pure or applied science; these grants are also made for a year, and may be renewed for a further four years. (iii.) Grants to a teacher engaged on research to enable him to employ a suitable assistant to help him in his research, but not in his teaching. (iv.) Grants in special cases to a worker investigating some new branch of science to enable a research lectureship to be established in a university, pending the provision of a suitable endowment from other sources. The Department has a close working agreement with the Royal Society, who administer a special Government fund for aiding research workers,

under which the two bodies work in concert, keep each other fully informed of the cases that come before them, and refer to the other those applications which appear to be more suitable for their consideration.

THE ORGANISATION OF INDUSTRIAL RESEARCH.

The second branch of the work deals with the encouragement of research in the industries. The Advisory Council recognised that many of our industries were making less use of science than was desirable, or indeed necessary, if they were to survive. But they realised that there were many causes for this. They refused to endorse the easy cry that manufacturers were too ignorant or too indolent to make use of scientific men. This may be one factor in some cases, but it is by no means the whole story. The Council attempted to analyse the position in their first annual report, and I need not repeat the analysis here. It will suffice to say that the relatively small size of the majority of British firms, the shortage of well-trained researchers and even of routine workers in science, and the lack of mutual understanding between the universities and the industries, were some of the difficulties in the road. The Council reached the conclusion that any safe advance must be made by the industries themselves, that the most hopeful means was co-operative action by the firms in each industry, and the best the Government could do was to encourage co-operation, while leaving the immediate responsibility to those who presumably knew most about the conditions of the industry, *i.e.*, to the manufacturers themselves. Thus the scheme for co-operative research associations came into being. These associations are limited liability companies working without profit and with a nominal guarantee from their members in place of shares. The members of each association make an annual subscription, usually proportionate to the size of their business, towards the income of the association, and when the memorandum and articles of the association have been approved by the Department and a licence has been issued by the Board of Trade, the Board of Inland Revenue recognises the subscriptions of the members as "business costs," *i.e.*, as free from income tax and excess profits duties. If, in the opinion of the Department, further help is needed, it will make an annual grant-in-aid to the association for a period of five years. This grant is in the first instance usually pound for pound, but the average over the whole five years will in most cases be less than this. The intention is to give the new associations an impetus over a period sufficiently long to enable them to prove the value of research. After that it is anticipated that they will need no encouragement to continue the good work.

The Department acts as a clearing-house of information for the associations, and gives all the assistance and advice in its power, whether the association is in receipt of a grant or not. The association has full control of its own income, whether from Government or from its members, and all the results of research are the sole property of the association held in trust for its members. The Department asks to be kept informed, acts as the go-between when an association seeks to sell its results to another industry or association, and reserves the power to prohibit the communication of results to a foreign body or person. But this is the limit of Government interference. The Advisory Council laid stress upon the representation of science as well as capital and management on the board of directors, and they think it desirable that there should be some representation, if possible, of skilled labour. They also lay great stress upon the appointment in each case of a responsible technical officer as director of research, in order to ensure the unity of direction which is as necessary in research as in the battlefield. Two other important points of detail should be mentioned. The scheme of the Advisory Council contemplates that the associations should be limited in each case to those firms in an industry or in a group of closely related industries whose interests are sufficiently homogeneous to

* Read before the Royal Society of Arts, February 12, 1919.

induce them to pool their resources for the purposes of research. It will not usually be feasible for both producers and users to combine in a single association unless, as in the case of cotton, the producers and users are so intimately related that the processes of each immediately affect the whole business of the other. The various non-ferrous metal trades can combine without difficulty. The different branches of the internal-combustion engine trade cannot. The problems of the aeroplane engine and the heavy Diesel motor are at present too remote from each other.

The second point is that the scheme contemplates the establishment of one association of each kind for the whole United Kingdom—not a series of local associations. Experience has shown that a number of local associations in the same industry would raise questions which would inevitably lead to Government interference, and that the number of competent research workers, and especially men fitted to be directors, is far too small to allow of this procedure. A single national association avoids this danger and has the important advantage of commanding larger resources as well as wider experience. On the other hand, where an industry is widely distributed over the three kingdoms provision is made for local branches and committees with large scientific autonomy, so as to allow the research undertaken to correspond with the variety of problems arising from local differences in material or processes or types of product.

That is the scheme in barest outline. There are four associations already at work, fifteen more are just coming into existence, and another eleven are in the earlier stages of formation—in all some thirty. You will realise that great elasticity in financial arrangement was necessary to allow the Government to make agreements suited to the varying conditions of the many industries of the country, and that it was desirable to give an indication from the outset that the grants made would presumably cease after a period of some five years. Accordingly the Advisory Council recommended the establishment of a special limited fund for this purpose, and you, my lord, induced the then Chancellor of the Exchequer to ask Parliament for a fund of a million sterling to be spent, both capital and income, in aiding approved research associations. The fund is held by the Imperial Trust for the Encouragement of Scientific and Industrial Research, a body of seven Cabinet Ministers to whom a Royal Charter has been granted to enable them to hold this and other property for the purposes of the Department.

THE ORGANISATION OF NATIONAL RESEARCH.

We may now turn to the third section of the field—which I have spoken of as the Organisation of National Research. You will have noticed that all the work already described is national in a sense, but it is work which the Advisory Council realised the Department had better delegate to authorities not itself. There remains a growing body of work which for one reason or another the Government must do itself, and this is what is meant by the phrase "National Research." The work in question may be divided into three subheads. Here again it will be seen that, leaving aside the function of intelligence which is a matter of orderly collection, collation, and distribution by competent officers acting in general conformity with the directions of the Advisory Council itself, the policy is one of delegation to persons specially qualified by their knowledge and experience to do the work in hand, with great freedom to initiate and carry out a scheme of work which they themselves have devised.

I. A Clearing-house of Information.

I have already referred incidentally to the function of the Department as a clearing-house of information for the industrial research associations. It similarly acts as a clearing-house for all the research organisations and workers with which it is officially connected. But it con-

fines itself to this. The Council has been urged from many directions during the last two years to establish or aid in establishing a great central bureau of scientific and technical knowledge to which all and sundry might come for information from all the world over, which bears upon any conceivable point of scientific or technical interest. The proposal has been most carefully examined and as decisively rejected. Such a bureau, which would be many times larger than the Institut Solvay at Brussels, would need the services of hundreds of scientific men and linguists. Even if its information could, at great expense, be kept moderately up to date, it would necessarily be in arrears of the knowledge of any scientific worker who is abreast of the literature of his own subject, and since it would be prepared by persons not themselves actively engaged in research or in industry would in many cases at least omit details of importance to one or other line of advance. For a detail of subordinate importance to one worker may be vital to the interests of another.

On the other hand, the workers of the research associations, the research boards, and research committees working officially under the Department will often be doing confidential work of great interest and importance to each other, and if there is not some central clearing-house the rate of advance will be much slower than it need be. This service the Department is undertaking, and it is likely, even when thus narrowly defined, to be a fairly big business. Moreover, the Department is slowly constructing a confidential register of research workers and their work for the benefit of the different organisations related to it, and, now that the great war services are being curtailed, an inventory of scientific apparatus and machinery of which the Government is anxious to dispose. It is also slowly forming a technical library, and hopes that this library, as well as a common room, may be used by officers and directors of the research associations for meeting each other, and discussing with officers of the Department matters of common interest.

II. Investigations carried out for other Departments of State.

The next subhead of National Research is far more important. It deals with investigations carried out for other Departments of State. It had been recognised from the beginning that if the Department were to initiate researches of its own on the advice of the Advisory Council without knowing the bearing they might have on the work or intentions of other Departments of State, confusion and worse than confusion might result. Accordingly, the Minister invited each Department of the Government to appoint one or more assessors to the Advisory Council. The assessors have the right to attend the meetings of the Council and receive the agenda papers and minutes of the Council. They also furnish the natural channel of informal communication between the Department of Research and the Departments they represent. This device has had the happiest results. The Council is informed from the first as to the attitude of the Departments concerned in any business which may arise, and difficulties are threshed out before proposals are formulated, and not after they have been adopted by the Department. Many Government Departments are engaged on research for their own purposes, and repeatedly the Council has deferred the consideration of proposed investigations which it learnt were engaging the attention of other Departments, even though the research might cover only part of the field, until the considered views of all parties concerned had been ascertained and unified. It has thus been possible on more than one occasion to remove overlapping already in existence, and to bring the workers under different Departments together into a co-ordinated plan of attack. The Council never knowingly enters a field of work already occupied, even in part, without previous agreement with the Departments concerned. The assessors on the Council have made this plan possible and easy. For more than a year past the Council has been similarly brought into

touch with research work in Canada by the presence at its meetings of Prof. McLennan, F.R.S., as assessor from the Canadian Advisory Council for Scientific and Industrial Research. But this is not all. The close understanding which has been reached with the administrative Departments of State has led them to request the Research Department to undertake for them a number of investigations which were less well suited for an administrative organ than for one like the Research Department, which is free from the embarrassments that administration of the law entails. Thus the Home Office invited the Department to investigate the question of mine-rescue apparatus. The first report of the committee established by the Advisory Council has proved on publication to be so valuable in directions hitherto unexpected, that the Commander-in-Chief in France asked that the committee might be placed in touch with General Headquarters. The Local Government Board invited the Department to undertake a series of researches into building materials in connection with the housing policy of the Government, and this led to similar requests from the Commissioners of Woods and Forests, as regards home-grown timber, from the War Office, and from the Board of Agriculture. So that from small beginnings a large body of researches into problems of building has been undertaken. These are but two examples out of many cases in which other Government Departments have welcomed the services which a Department of Research can render. The Advisory Council usually invites each Government Department concerned to nominate one of its technical officers to serve on any committee it may appoint to conduct research at the Government expense and for Government purposes, whether the proposal emanates from themselves or from some other Department. But it never appoints an administrative officer to a research committee or to the research boards of which I am going to speak, for it is in their view essential to avoid any idea that the findings of a committee or board have been in the slightest measure the result of administrative policy. The findings of the committee must be taken on their merits, and the administrative Department or Departments concerned are free on their own responsibility to adopt or neglect them as they may find necessary or desirable. Nevertheless the Council is prepared when it is so desired to appoint administrative officers from the Departments concerned as assessors to a research committee or board, in order to keep the administration in touch with the direction in which the committee is moving—often a useful arrangement.

III. Research Boards.

When a large group of researches has to be undertaken in the national interest and an elaborate organisation for research has to be set up, the Advisory Council has recommended the Minister to give the research committee a more independent status, and to place it in closer relation to himself. This is the third type of organ for national research, and is called a research board. The work done by boards is not only wide in scope and complex in organisation, but it is always work which for one or more reasons is not susceptible of organisation by an autonomous body like a research association. It is also work which must, because of this, be paid for altogether or almost altogether by the taxpayer. The first board of this kind to be established was the Fuel Research Board. Fuel and economy in its use affect the poorest worker in the land as intimately as the largest consumer. Fuel is the basis of all our industries and of our supremacy at sea. No association of manufacturers could be expected to attack so wide a range of problems in all its parts. The cheapest and fairest way of distributing the burden was to place it on the shoulders of the taxpayer. In a word, this was a typical piece of national research. The same arguments apply to the preservation of food as to the conservation of coal, and at a later date Lord Curzon established the Food Investigation Board to deal with this vastly important group of problems.

The Advisory Council had been considering the question of fuel at the earliest of its deliberations, and the report of Lord Haldane's Coal Conservation Committee made definite recommendations which led directly to the establishment of the Board. In the case of food the impetus came first from the Ministry of Food and the Board of Agriculture and Fisheries, both of which Departments were deeply concerned in the feeding of the people. Similarly, it was the Secretary of State for Home Affairs and the Medical Research Committee which, severally and within a single week, invited the Advisory Council to take up the question of industrial fatigue. This led to the establishment of the Industrial Fatigue Research Board, which apart from the importance of its special field of work, is interesting because it was appointed jointly by the Research Department and the Medical Research Committee. One further example of a research board must suffice in illustration of this part of the Department's work. I refer to it not only because of its inherent importance, but because it shows the elasticity which the policy thought out by the Advisory Council permits. The Government decided to assume responsibility for the National Physical Laboratory as from March 31st last, on the invitation of the Royal Society, who had previously been responsible for its maintenance. The Laboratory had been administered since its inception by an executive committee appointed by the Society under the terms of a scheme approved by the Treasury, who made it an annual grant in aid. It was found on investigation that all the powers of scientific control exercised by the Royal Society through the executive committee could be continued if the executive committee were taken over as a research board by the Department. Accordingly this was done. The growth in the importance of the Laboratory during the war will be realised when you remember that the total income of the Laboratory in 1913-14 was £43,713 6s. 10d., while the amount taken for the Laboratory in the estimates of the Research Department for the coming year, 1919-20, is £154,650.

The responsibility and initiative entrusted to a research board are very great. When the Minister has appointed a research board on the recommendation of the Advisory Council, the board is invited to prepare a scheme of work and a budget of expenditure. These are submitted to the Minister together with any remarks upon them the Advisory Council may wish to make. The Council does not amend the scheme or estimates of a board, for research boards are responsible directly to the Minister and their chairmen have immediate access to him. The less important research committees are appointed by the Council itself, and are subject to its control both in their schemes of work and their proposed expenditure. The recommendations which go to the Minister are recommendations of the Council, not of the committees. But both research boards and committees, when once their proposals are approved, have full power to expend the appropriations made to them, subject only to the rules imposed upon all public expenditure by Parliament.

THE PRINCIPLE OF DELEGATION.

The research boards and committees consist of men of science, men of business, and technical officers of the Government Departments concerned. They prepare schemes of work, select the researcher and determine the amount of his remuneration, but they do not as a rule conduct research themselves. They are executive bodies. The Advisory Council is not executive, but deals with general policy. Here again it will be seen that the procedure has been to delegate authority, even in the case of research carried out by the Government for national purposes to bodies of experts. It is a commonplace among administrators to fear the expert, and there is no doubt that, taken singly, he may be a very embarrassing and even dangerous being, but he is far less dangerous when he works with other experts of his own kind. If in addition the experts are confined to their own "expertise," as it has

been called, they are no more dangerous than other able men, and, as might have been expected, they do their own work better than others can do it for them. It was well said some years ago that the main problem which Government Departments would have to solve in the present century was how to use the expert. The Research Department is an experiment in this direction. The attempt to differentiate the work of the Department according to function, and give each class of work to the appropriate type of worker, has not only secured the strenuous assistance of the man of science and the man of business, each contributing from the fulness of his own knowledge, but it has greatly strengthened the position of the Civil servant whose business is administration. It has strengthened it because it has limited his responsibility to the matters which belong to his kingdom. The administrative head of the Department has no power to advise his Minister upon the scientific policy to be pursued, and it would be improper for him to do so, were he the most distinguished man of science in the country. Since he is only an administrator he is under no such temptation. If the scientific initiative emanates from the Minister himself or from another Department it stands referred to the Advisory Council. All other initiative derives from the Council itself. The duty of the Administrative Civil servant is to advise the Council and the Minister of the bearing which any proposed line of action will have upon the work of other Government Departments and especially the Treasury, or upon the attitude of Parliament, or upon the finance of the Department. He has to deal with questions arising in the House and with the machinery by which the work of the Department is regulated. Finally, the Civil servant is responsible under the Accountant-General for the supervision of all expenditure and of all property held by the Imperial Trust, including patents, and funds held in trust for the Department. Here is plenty—which may properly engage the best energies of a well-trained staff of Civil servants. Lord Haldane's Committee on the machinery of government which has recently reported to the Minister of Reconstruction, sees in the experiment I have tried to describe the germ of what may ultimately become a great Department of Research and Information, influencing every administrative organ of the State, because it is the servant of them all. Be that as it may, the mere suggestion is an acknowledgment of the courageous faith with which the Government in 1915 set out upon this particular adventure, in reliance on the law that sound organisation is always based upon the proper differentiation of function.

To sum up. The activities of the Department are exercised in three main directions. First, it seeks to encourage the worker in pure research by looking for him in the places where he is most likely to be found, through the eyes of individual men and women who are themselves engaged in research and teaching others how to begin. When the man or woman has been found who needs assistance, they receive it in liberal measure, with no restrictions beyond the necessity of showing that they are continuing their work. Secondly, the Department is helping the firms in different industries to co-operate, with a view to raising the funds necessary for employing first-rate men of science in the solution of the problems with which they are faced and in the scientific development of the industry in question. In this connection the Department is building up a clearing-house of information for the benefit of all concerned. Finally, the Department is offering its assistance, on the other hand, to other Government Departments who desire to have research undertaken on a scale and for purposes which they cannot themselves easily compass. On the other hand, it is organising research into problems of practical utility, which are of such wide importance that they cannot be handled by any one section of the nation. In both regards it proceeds by delegating the responsibility for the conduct of this work not to officials but to boards of experts, who are entrusted

with the preparation of the scheme of work, the employment of the workers, and the control of its execution. The principle, as you will see, throughout is the same—the principle of delegation to those best fitted for the work in hand.

THE CASE FOR A RING ELECTRON.*

By Dr. H. S. ALLEN.

For many purposes it is sufficiently accurate to regard the unit of negative electricity as a point charge, but for a more exact determination of its properties it is necessary to assign some definite shape to the distribution of electricity constituting the electron. Thus the shape is often assumed to be that of a sphere or spheroid. Although the spheroidal form possesses advantages from the standpoint of mathematical analysis, there are many reasons why it is preferable to assume that the electron is in the form of a current circuit which can produce magnetic effects. Then the electron, in addition to exerting electrostatic forces, behaves like a small magnet. In its simplest form the magnetic electron may be looked upon as a circular anchor ring of negative electricity which rotates about its axis with a velocity which is certainly large, and is perhaps comparable with that of light. Parson has suggested that the name *magneton* should be applied to this electron (*Smithsonian Misc. Coll.*, 1915, lxx., No. 11); but, as this term has already been employed in a somewhat different sense, I prefer to speak of the ring electron.

With reference to the corpuscular theory of light, Sir Isaac Newton wrote:—"I shall not assume this or any other hypothesis, not thinking it necessary . . . yet, while I am describing this to avoid circumlocution and to represent it more conveniently, I shall speak of it as I assumed it and proposed it to be believed." In collecting the arguments in favour of the ring electron I do not wish it to be understood that I am in agreement with them all or with the views of all those who have supported this hypothesis. Some of the arguments have been well stated in Parson's paper on a magneton theory of the structure of the atom.

PART I.—THE ARGUMENTS FOR A RING ELECTRON.

1. *Loss of Energy by Radiation.*—The most important difficulty in connection with the classical electron is that of the radiation which must take place, according to the laws of electrodynamics, when the electron (or a number of electrons) is circulating in an orbit. This difficulty, though perfectly well known, is usually ignored altogether in the discussion of atomic theories. When the number of electrons in the orbit is increased the loss of energy is greatly diminished, and the difficulty may be met to a certain extent by postulating rings containing many corpuscles. We now know, however, that in the case of the lighter atoms—hydrogen, helium, lithium—the number of electrons is small; in fact, it appears certain that Moseley's atomic numbers, $H=1$, $He=2$, $Li=3$. . . must be accepted as representing the number of electrons in the atom. The only way left of meeting the difficulty for the classical electron is to postulate such a "binding" of the electron to the nucleus as precludes radiation in the stationary state of the system (Bohr). This is, of course, purely hypothetical, and it is certainly simpler to do away with the difficulty altogether by assuming the rotation of an annular charge. Radiation will then occur only in the case of disturbances or irregularities in the annular motion.

2. *Diamagnetism.*—The second objection to the prevailing theory arises in connection with the explanation of

* Opening Paper on a Discussion on "The Case for a Ring Electron," at the Imperial College of Science, October 25, 1918. From the *Proceedings of the Physical Society*, xxxi., Part 2.

diamagnetic atoms—and most substances are diamagnetic. In order to account for a zero resultant magnetic moment, the independent orbits must be considered to have their axes uniformly distributed in three dimensions. Interference between separate rings of this sort would result in an altogether chaotic motion in the atom. Whilst such chaotic motion would be consistent with diamagnetism, it would invalidate all those considerations which presuppose the existence of definite periods of vibration in the atom. The question is discussed at some length in Parson's paper. The substitution of the ring electron for Langevin's electron in orbital motion removes the fundamental difficulties of his theory, but leaves the superstructure almost intact. That this substitution can be made clear by a short quotation from the conclusion of his paper:—

"... and we can form a simple and exact picture of all the facts of magnetism and of diamagnetism by imagining the individual currents produced by the electrons to be indeformable but movable circuits of no resistance and very great self-induction, to which all the ordinary laws of induction are applicable."

3. *Paramagnetism*.—In the older theory there are certain outstanding difficulties in connection with the explanation of paramagnetic properties. No satisfactory explanation has yet been given as to how the orbits become tilted under the influence of an external magnetic field. Although it may not be easy to develop a complete mathematical treatment of the behaviour of the ring electron in a magnetic field, it would certainly seem easier to understand the tilting of such a system than that of a single particle moving in a closed orbit.

By means of X-ray photographs showing the Laue diffraction pattern for crystals of magnetite, hematite, and pyrrhotite in the magnetised and unmagnetised state, K. T. Compton and Trousdale came to the conclusion that the atoms do not leave their positions of equilibrium during magnetisation (*Phys. Rev.*, 1915, v., 315). These results may be regarded as consistent with any form of the electron theory of magnetism, but the hypothesis of ring electrons seems to afford a particularly clear and straightforward explanation of the phenomenon.

A further step in the analysis was taken by A. H. Compton and O. Rognley, who examined the intensity of the reflected beam of X rays reflected from a crystal face (*Phys. Rev.*, 1918, xi., 132). In no case was any change observed in the intensity of the reflected beam when the crystal was magnetised or demagnetised, though the method was sufficiently sensitive to detect a variation in the intensity of less than 1 per cent. Since the intensity depends upon the arrangement of the electrons in the atoms which make up the crystal the authors conclude that it is neither a group of atoms, such as the chemical molecule, nor the atom itself which is the elementary magnet. We must look to the atomic nucleus, or to the electron for the ultimate magnetic particle.

The existence of a zero point energy of rotation is supported by the magnetic susceptibility of paramagnetic substances. According to Osterhuis (*Phys. Zeit.*, 1913, xiv., 862) most of the deviations from Curie's law found at low temperatures may be explained quantitatively on this assumption. This view has been supported by Keesom (*Konink. Akad. Amsterdam*, 1913, xvii., 454, 468). It receives a natural explanation if the ring electron be accepted, for the electron would retain its magnetic properties at low temperatures.

The existence of a mechanical effect accompanying magnetisation was foretold by Richardson in 1908 (*Phys. Rev.*, 1908, xxvi., 248). Assuming that the resultant magnetic fields which the atoms of magnetic (as opposed to diamagnetic) substances possess, arise from the motion of their constituent electrons in closed orbits, there must be a moment of momentum per unit volume proportional to the intensity of magnetisation. Einstein and De Haas (*Deutsch. Phys. Gesell.*, 1915, xvii., 152) succeeded in observing the effect predicted by Richardson, and obtained a factor of proportionality corresponding to that which

would be due to negative electrons. Experiments at Princeton by Stewart led to a value only one-half of that obtained previously (*Phys. Rev.*, 1918, xi., 100). The magnitude of this momentum can be accounted for if positive, as well as negative, charges are moving within the atom, but in opposite directions. A similar result was obtained in the work of S. J. Barnett, who showed that a rotating cylinder of iron becomes magnetised (*Phys. Rev.*, 1915, vi., 239). This may be regarded as the converse of the Richardson effect. The relation of these phenomena to the properties of the ring electron has been discussed by Webster (*Phys. Rev.*, 1917, ix., 484).

4. *The Asymmetry of certain Types of Radiation*.—In order to explain the asymmetry of scattered X-radiation, A. H. Compton (*Journ. Wash. Acad. Sci.*, January 4, 1918) has examined theoretically the scattering to be expected when the electron is in the form of a spherical shell, each part of which can scatter independently and may be capable of rotational motion. He found that it was then possible to explain not only the asymmetry of the scattered rays, but also the diminution of scattering with decrease of wave-length. Since the mass of an electron cannot be accounted for on the basis of a uniform distribution of electricity over the surface of a sphere Compton suggested that the true shape of the electron may be that of a ring. His estimate of the radius is 2.3×10^{-10} cm., but reasons have been given for supposing that this estimate must be reduced to about one-tenth of the value stated (*Nature*, 1918, c., 510).

The same kind of asymmetry occurs in the case of corpuscular radiation excited when X-rays fall on a thin plate of any material. E. A. Owen (*Proc. Phys. Soc.*, 1918, xxx., 133) has recently carried out experiments which show that no difference can be detected between the ratio of emergent to incident corpuscular radiation when the screen from which the corpuscles are ejected is changed from the crystalline to the amorphous state. This result renders doubtful the explanation of asymmetry put forward by H. A. Wilson, who attributed it to the difference between the behaviour of crystalline and amorphous material, and suggests that an explanation of a more fundamental character is necessary to account for this phenomenon. This view is supported by the fact that the ratio of emergent to incident corpuscular radiation is approximately the same for the two salts investigated and for the metals, gold and silver. It would appear that the asymmetry must be due to some property of the electron itself and not of the atom from which the electron is liberated.

5. *Absorption of X-rays by Magnetic Substances*.—It has been observed by A. H. Forman (*Phys. Rev.*, 1916, vii., 119) that iron has a slightly greater absorption coefficient for X-rays when magnetised parallel to the transmitted beam when unmagnetised. (In Faraday's notebook is found the suggested query:—"Does this [magnetic] force tend to make iron and oxide of iron transparent?") This may be attributed to the fact that when the axis of the ring electron is parallel with the incident X-rays the energy scattered by the electron is a maximum (A. H. Compton).

6. *Ionisation of Gases by X-rays*.—It has long been known that the ionisation produced in a gas by Röntgen radiation or ultra-violet light is remarkably small; when the ionisation is strong the ratio of the free ions to the number of gas molecules is less than 1 : 10¹². This may be explained by some form of the unitary theory of light, but an alternative explanation may be suggested to the effect that there may be only one plane in which the electrons can absorb sufficient energy from the Röntgen ray for ionisation (*cf.* A. H. Forman, *loc. cit.*).

These ideas may have some bearing upon the work of Righi on the ionisation of gases by X-rays in a magnetic field (*R. Accad. Sci.*, Bologna, 1916-1917, iv., 1; 1917-1918, v., 3). Experiments carried out under very varied conditions led to the conclusion that the magnetic field tends to favour ionisation of a gas by diminishing the

energy required. Thus an ion or an electron in motion can ionise a gaseous atom on collision, when a magnetic field exists, although the kinetic energy of the electron does not reach the minimum value that is necessary in the absence of the magnetic field. This effect is termed "magneto-ionisation."

7. *Thermo-electric Effects.*—Grondahl claims to have obtained experimental evidence for the existence of an electron endowed with a magnetic moment (*Phys. Rev.*, 1917, x., 586). Such an electron would be affected by a non-uniform magnetic field. A conductor placed in such a field would therefore gain a negative potential in that part which lies in the stronger portion of the field. A magnetic field should produce an effect on the thermo-electric force of magnetic substances. This effect was examined in the case of a copper iron couple, the iron member of which was a short wire which could be placed in a magnetising coil. Theory predicts an increase in the thermal E.M.F., and this was actually observed and found to be of the order of magnitude to be expected.

8. *The Radiation Formula of Planck.*—A method of deducing Planck's radiation formula by making certain assumptions as to the internal mechanism of Parson's "magneton" has been given by Webster (*Ann. Acad. Proc.*, 1915, l., 131; *Phys. Rev.*, 1916, viii., 66). Energy is stored in the rotating ring in a non-radiating form. "If the electricity is movable on the ring in any other way than as a rigid mass, the alternating external force of a light wave will induce oscillations on it capable of absorption and radiation of energy. These induced oscillations were shown to give an explanation of refraction, diffraction, and allied phenomena almost exactly like that of the classical electron theory. At the same time the internal mechanism assumed above for transferring energy between the oscillations and the circulation can be supposed to damp the induced oscillations, transferring their energy to the rotation, until the energy accumulated above the initial value reaches some definite multiple of the quantum. At such a point it is assumed that the process may be reversed, starting a large oscillation, which will be maintained constant at the expense of the circulation, until the excess energy is all radiated away. The probability, η , that such an oscillation will start when the stored energy reaches a given multiple of $h\nu$ is given by Planck's condition $(1-\eta)/\eta = p/l$, where l is the mean square of the electric field per unit frequency interval, and p is determined so as to give the Jeans-Rayleigh law at low frequencies. The entropy of the system is then found by Planck's equation $S = k \log W$, where the microscopic state of a system is determined by the total accumulated energy of each oscillator. The derivation of Planck's law in this theory is therefore almost exactly like his."

Attention may again be drawn to the significance of Planck's constant, h , which may be regarded as a quantum of action. The view, first suggested by Nicholson, that h represents an angular momentum is simpler and easier to realise. McLaren identified the natural unit of angular momentum with the angular momentum of the magneton, and it has been pointed out several times that this implies proportionality to the magnetic moment of the magneton. Thus the ring electron serves to give an intelligible meaning for this "universal" constant, and at the same time suggests the possibility of a relation between h and e . Such a relation has in fact been put forward by Lewis and Adams in the form—

$$15c^2 h^2 = 8\pi^2 (4\pi e)^2,$$

an equation based on a certain assumption as to the form of the constant in Stefan's law of radiation.

9. *Series of Lines in Spectra.*—The theory of line spectra proposed by Bohr has met with a considerable amount of success in connection with the hydrogen spectrum, and the developments made by Sommerfeld and others have afforded an explanation of the fine structure of the hydrogen lines. It may prove possible to restate Bohr's theory, and, whilst retaining its essential features,

modify it so as to apply it to the case of the ring electron. Thus it might be suggested that the "stationary state" of the electron in its orbit corresponds to a particular value of the radius of the annular electron, the change from one stationary state to another corresponding to a definite change in the radius. It would, of course, be necessary to introduce some hypothesis to fix the size of the ring, just as it is necessary to postulate the stationary state in Bohr's theory. In the last named theory no detailed assumptions are made as to the mechanism of transition between two stationary states or as to the mode of emission of radiation. In the case of the ring electron radiation might arise from pulsations of the ring in its passage from one stationary condition to another. In this connection it is interesting to recall the views of Sutherland with regard to the origin of lines in spectral series (*Phil. Mag.*, 1901, ii., 245). He came to the conclusion that the series might arise from kinematical considerations, and explained them by considering the nodal sub-divisions of a circle.

It may be well again to draw attention to the fact that, as shown by Nicholson, coplanar rings of electrons are not possible when electrostatic forces alone are taken into consideration. Provided the electrons are in one plane they must form a single ring. The assumption of rings of electrons is no longer required if both electron and core are endowed with magnetic properties, as the electrons may then be supposed to take up positions of statical equilibrium with reference to the core—a condition of affairs which is in harmony with the facts of chemical combination and crystalline formation.

(To be continued).

HANDY FACTORS.

By ELTON A. NASH.

MAKING use of the following factors will be found to be quicker than looking up tables, or perhaps of even taking the bother to weigh off factor weights of the substances being tested. Perhaps the results will not be accurate to the third place, but are accurate enough for ordinary works practice.

To convert BaSO_4 to S, multiply by 11, divide by 80.

To convert ammonium phosphomolybdate to P, multiply by 33 $\left(\frac{11 \times 3}{\text{factor}} \right)$ divide by 2000.

To convert ammonium phosphomolybdate to P_2O_5 , multiply by 3, divide by 80.

Example 1.—S in coke, pyrites, burnt ores, &c.

Weight of substance taken		1 grm.	0.5 grm.	0.25 grms.
		(say coke)	(say pyrites)	(say burnt ore)
Weight of BaSO_4 found	0.0824	1 696	0.782	
	824	1696	782	
	80.9064	418 656	218 602	
Result	1.133	46.64	4.301	
	per cent	per cent	per cent	

Example 2.—P in steel, basic iron, &c.

Weight taken		2 grms.	0.5 grm.
		(say steel)	(say basic iron)
Weight of yellow precipitate	0.096	0.564	
	96	564	
	1056	6204	
	43168	18612	
Result	0.0792 per cent	1.86 per cent	

Example 3.— P_2O_5 in basic slag, &c.

Weight taken	0.25	1 grm.
	(say basic slag)	(say iron ore)
Weight of yellow precipitate	1.046	0.162
	2)3138	8)486
Result.. .. .	15.69 per cent	0.61 per cent.

VOLUMETRIC DETERMINATION OF
REDUCING SUGARS.*A SIMPLIFICATION OF SCALES' METHOD FOR TITRATING
THE REDUCED COPPER WITHOUT REMOVING IT FROM
THE RESIDUAL COPPER SOLUTION.

By W. BLAIR CLARK

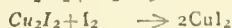
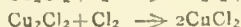
Biochemist, Cotton, Truck, and Forage Crop Disease Investigations,
U.S. Department of Agriculture.

ONE who contributes to the now voluminous literature of reducing sugar determinations must show a good excuse for his temerity. Especially is this so in view of such exhaustive investigations as have been conducted in recent years by Benedict (1), Kendall (2), and Peters (3), to cite these only among the many workers who have addressed themselves to the subject in this country and abroad. The writer would not essay to add to this list did he not feel that the technique which he proposes is accurate and at the same time decidedly simpler than any which has appeared hitherto.

Methods such as Fehling's, Pavy's, and Benedict's, wherein the test solution is added from a burette in just sufficient amount to reduce a given weight of copper all involve titrating a boiling liquid, and all are also likely to necessitate a wide range in the volume of titrating liquid required to reduce the copper, since irrespective of its concentration there must be added a quantity of reducing sugar corresponding to the weight of copper used. In addition to these inconveniences the end-point is rather difficult to ascertain with certainty in the Fehling method, while the Pavy method involves a somewhat complicated set-up of apparatus for either routine or occasional analyses. The Benedict method is a decided improvement over either of the other types, but still leaves some things to be desired.

In the other group of copper reduction methods, a part only of the copper being reduced and this fraction then determined volumetrically or gravimetrically, the necessity for filtration and washing of the cuprous oxide is added to whatever other processes may be involved. It is true that Maquenne (4), Lehmann (5), and others have proposed the titration of the residual copper without removal of the cuprous oxide, but the method has never become popular. Many of these variations also require such quantities of potassium iodide as to make the expense a serious item when numerous analyses are to be made.

F. M. Scales (6) has published a method in which the cuprous oxide is dissolved without removal from its mother liquor by the addition of hydrochloric acid, and the resulting cuprous chloride then treated with an excess of standard iodine solution, the excess being determined by titration with sodium thiosulphate. The oxidation may be more complicated than indicated herein, but from the fact that upon the addition of the iodine a white precipitate is at first formed, which then dissolves as the excess of iodine flows into the mixture, the following reactions would seem to occur:—



The cuprous chloride formed in the first reaction is soluble in the mixed sodium tartrate or citrate and chloride solution in which the reaction occurs.

Scales used the ordinary Fehling solutions, carrying out the reduction in a beaker according to directions of Munson and Walker (7), then transferring the hot mixture to a volumetric flask containing the necessary amount of hydrochloric acid for solution of the cuprous oxide, making up to volume, and withdrawing an aliquot part for treatment in another flask with diluted iodine solution, this being followed by titration of the excess iodine.

When the writer first tried this method he was unable to obtain a satisfactory end-point. The blue colour returned almost instantly. It was determined when taking the method up again later that this was due to too great an excess of hydrochloric acid, which reacted with the potassium iodide of the iodine solution to liberate more iodine, a result of not having followed Scales' concentrations exactly. Furthermore, making the solution up to volume, mixing and pipetting out while still hot is undesirable both from theoretical and practical considerations.

Cambridge (8) in adapting the method to clinical use substitutes for the Fehling solution a modified Benedict solution, and dissolves the cuprous oxide before removal of the mixture from the beaker in which the reduction takes place. While working with this modification of the method it was found that the entire process might conveniently be carried out in a single vessel with practical exclusion of the air from the time reduction of the copper begins until after it has been reoxidised by the iodine. As a result the simplified procedure described in later paragraphs has been developed.

The writer has worked out concentrations, volumes, and conditions suitable for use up to approximately 60 mg. of reducing sugar. Workers desiring to determine larger quantities may modify and standardise the various factors to suit their conditions. The experimental data here presented should make plain the principles to be followed in making modifications. It is to be noted that there is no table to be referred to in calculating results. Each manipulator standardises both his conditions and his solutions by means of known solutions of pure dextrose, invert sugar, starch, or whatever reducing substance he may have occasion to handle.

A. The Solutions Used.

1. *Alkaline Copper Solution.*—As already stated a modified Benedict solution is used. It is made up according to the following formula:—

	Grms.
Copper sulphate crystals .. ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	16.0
Sodium citrate crystals .. ($2\text{Na}_3\text{H}_5\text{O}_7 \cdot 11\text{H}_2\text{O}$)	150.0
Sodium carbonate anhyd. .. (Na_2CO_3)	130.0
Sodium hydrogen carbonate anhyd. (NaHCO_3)	10.0

Water to make a final volume of one litre.

The copper may be dissolved separately in 125 to 150 cc. of water; the remaining solid constituents in about 650 cc. water, heating to accelerate solution. When all are in solution pour the copper solution slowly into the other with stirring, make up nearly to volume, cool, complete the volume to one litre and filter. None of the weighings or measurements need be made with extreme accuracy.

The sodium hydrogen carbonate is added to help insure a non-oxidising atmosphere in the reduction flask. The solution will carry more copper, but the amount given is sufficient to accompany convenient volumes of thio-sulphate and iodine solutions in standard concentrations from tenth to fiftieth normal. This solution keeps well, though perhaps not indefinitely, as a small amount of sediment has been found in solutions some months old. Besides better keeping quality this solution has the advantages of greater sensitiveness to reducing sugars and less sensitiveness to sucrose than those in which sodium hydroxide is used, while the copper reduced under standardised conditions is very nearly proportioned to the quantity of reducing sugar present through quite a wide range in concentration of the latter.

2. *Iodine Solution.*—In the writer's work approximately 0.05 N solution has been found the most convenient concentration, although either 0.1 N or 0.04 N may be used. Dissolve 6.3 grms. resublimed iodine in 12 to 15 cc. of potassium iodide solution containing about 9 grms. of the

iodide. After solution of the iodine the volume is made up to one litre.

3. *Sodium Thiosulphate Solution.*—0.04 N is a convenient strength to use. 10.0 grms. thiosulphate crystals per litre make a solution of approximately this concentration. When possible new solutions are made up long enough in advance to stand two or three weeks before being standardised, as there is then little change in strength if evaporation is prevented (9).

Under the reducing conditions adopted by the writer one cc. 0.04 N solution is equivalent to approximately 1.2 mg. invert sugar. For still greater sensitiveness 0.02 N will give a satisfactory end-point, while 0.1 N may be used if the quantities of reducing sugar to be determined habitually exceed 50 to 60 mg.

4. *Starch Solution.*—This may be made of approximately 0.5 per cent concentration from either the commercially prepared "soluble starch" or from ordinary starch by the usual method of cooking. In the writer's routine work no attempt is made to use a preservative, as fresh solutions are made quickly when needed—usually twice or thrice weekly.

5. *Hydrochloric Acid.*—The concentrated C.P. acid of about 1.19 specific gravity is used.

B. Apparatus Used.

No special apparatus aside from the ordinary laboratory equipment is required. One will have occasion to use 5, 10, 20, and 25 cc. pipettes, 10 and 50 or 100 cc. graduated cylinders, and a 25 or 50 cc. burette. For routine work this latter should be connected with the thiosulphate bottle for automatic filling.

The reductions are carried out in a 200 or 250 cc. Erlenmeyer flask with wide enough mouth to take a No. 5 or 6 rubber stopper. It is well to select two or three flasks of as nearly the same weight as possible, then determine by several trials their relative heat conducting values. To do this pass a thermometer through one hole of a two- or three-hole stopper of the right size and adjust it so that the bulb just clears the bottom of the flask. Measure 30.0 cc. distilled water into the flask, replace the thermometer and heat over a flame so adjusted as to bring the temperature to 95° in about three minutes. After getting the heat properly adjusted repeat several times with each flask, noting the time to the nearest second. If the flask do not prove to be substantially equivalent it will be necessary to standardise the conditions separately for each one used. Each reduction flask is fitted with a two- or three-hole stopper, through one hole of which passes a thistle tube or Gooch crucible funnel, of which the tip of the stem has been drawn down so as to allow 50 cc. of water to flow through it from twenty-five to thirty seconds. In doing this the stem should be left of such length that with 80 to 85 cc. of liquid in the flask and the tip of the funnel dipping just beneath the surface, the body of the funnel will come within one or two centimetres of the stopper.

As a source of heat either a Bunsen burner or an electric hot plate may be used. The latter will be found more convenient if the voltage remains fairly constant; but if this is subject to much variation the fact will be reflected in the results.

On the electric hot plate used by the writer, with a certain 200 cc. Jena flask containing 30.0 cc. of the reaction mixture, and voltage of the heating current normal, boiling begins quite uniformly at three minutes and fifty to fifty-two seconds. Were a Bunsen burner being used it would be adjusted to reach this result in forty to forty-five seconds less time and a total heating period of five minutes instead of six would be used. In general, whatever the source of heat, one must standardise his conditions with sufficient definiteness to be readily reproducible. This whole subject of heating power has been admirably worked out by Peters (10), and need not be discussed further here.

C. Details of Procedure.

A solution containing the reducing sugar or sugars to be determined may be prepared in accordance with any of the usual methods described in the literature. Solutions which have been subjected to acid hydrolysis should be nearly neutralised with alkali hydroxide or carbonate.

In case there is reason to suppose that 10.0 cc. of the solution as finally prepared for test contains not more than 30 mg. reducing sugar, measure 20.0 cc. of the copper citrate-carbonate solution and 10.00 cc. of the test solution into one of the reduction flasks, insert the stopper with funnel or thistle tube prepared as previously described, and place over the source of heat, regulated as for comparing the flasks. Boiling should begin in three or four minutes and should continue for a definite time, say two minutes, so that the total time of heating ranges from five to six minutes. The exact period of heating is not material, but it is quite essential that both the period of heating and the heating power remain constant for any series of determinations which depend upon the same standardisation of the thiosulphate solution.

While the above mixture is heating, measure out about 60 cc. distilled water and 4.6 to 4.8 cc. conc. hydrochloric acid. Just enough acid is required to neutralise the alkali carbonate, dissolve the precipitated cuprous oxide, and render the resulting solution distinctly acid to litmus.

When the reduction mixture has boiled for the proper length of time, remove from the heat and immediately add through the funnel a few drops of the hydrochloric acid (11). Cool under the tap to approximately room temperature, adding the remainder of the acid, a few drops at a time to avoid loss of any appreciable quantity of it by volatilisation with the escaping carbon dioxide. When all of the acid has been added shake the flask sufficiently to insure thorough admixture of the contents and complete solution of the cuprous oxide. There should now be a clear, light green solution, provided the test solution was not highly coloured. Next, add (also through the funnel) about half of the 60 cc. water previously measured. If the funnel is properly adjusted this should result in covering its tip to a depth of from 1 to 3 mm. Next add an accurately measured quantity of iodine solution equivalent to 1.00 cc. approximately normal solution (12).

In adding this let the tip of the pipette rest in the neck of the funnel, then pour a few cc. of the remaining water into the funnel to make a water seal that will prevent air being drawn into the flask with the iodine solution. When the iodine has drained from the pipette remove the latter and rinse down the funnel with the balance of the water. If there is much cuprous chloride present in the solution, the first portions of the iodine will produce a white precipitate of cuprous iodide, which later is oxidised to cupric salt by the excess of iodine and dissolves. Should any of this precipitate remain undissolved it indicates an insufficiency of iodine and more must be added, in measured amount. Mixture of the contents should be accomplished by a gentle rotary motion of the flask rather than by violent agitation. According to the excess of iodine present the colour of the solution will now range from a light emerald-green to a dark brown, the former indicating a very small excess of iodine.

The funnel and stopper may next be removed and the solution immediately titrated with 0.04 N sodium thiosulphate (13) to determine the excess of iodine.

Starch solution as indicator need not be added until the solution has acquired a light emerald-green tint, a measured quantity of 2 or 2.5 cc. being then used. As the end-point is approached the deep blue of the starch-iodine complex becomes less and less dense until there is a sudden change from blue to green. Even with 0.02 N thiosulphate a single drop is sufficient to show this change and there should be no difficulty in recognising it, except possibly by those who do not readily distinguish between blues and greens. The difference between the cc. of thiosulphate used and the volume required by a blank test in which water instead of the substance under examination

is used with the copper solution, gives the thiosulphate equivalent to the iodine consumed in oxidising the copper reduced by the sugar.

The thiosulphate solution may be standardised by carrying out an exactly similar test in which a known quantity of invert sugar (20 to 30 mg.) or dextrose is used. From the data of this test one can calculate the milligrams of invert sugar or dextrose equivalent to 1.00 cc. thiosulphate solution, and use this factor in calculating the results with unknown solutions. The value of the factor varies somewhat for very small amounts of reducing sugar, hence it is advisable to carry out standardisations with approximately the same quantities of reducing sugar as are found in the samples to be analysed (see Table II. *prox.*).

This standardisation must be made each time a new lot of thiosulphate or iodine solution is introduced and also, in routine work, at weekly intervals.

If one prefers to use larger quantities of material the reduction may be carried out in 300 or 500 cc. flasks, using 40 cc. to 75 cc. copper citrate-carbonate solution and corresponding volumes of the test solutions and iodine. Where the quantities of reducing sugar habitually exceed 45 to 50 mg., 0.1 N thiosulphate solution may be used without sacrifice in the relative error. On the other hand, if one has material in which the reducing sugar in a convenient aliquot seldom exceeds 15 mg., it will be advisable to use 0.02 N thiosulphate with correspondingly less iodine for oxidation of the reduced copper. That which is to be kept in mind when dealing with any of these variations is that within the general limitations outlined each individual may re-standardise his conditions to suit the kind and quantity of material under investigation.

When engaged on routine work one operator, using a single reduction flask, can complete about four tests per hour; using two flasks he should be able to make six or seven tests per hour. In this case the contents of one flask will be undergoing reoxidation and titration while the other is being reduced. This estimate does not include the time spent in preparing the sugar solutions.

Notes.

1. Stanley R. Benedict, "The Detection and Estimation of Reducing Sugars," *Journ. Biol. Chem.*, 1907, iii., 101; "A Method for the Estimation of Reducing sugars," *Ibid.*, 1911, ix., 57.
2. E. C. Kendall, "A New Method for the Determination of the Reducing Sugars," *Journ. Am. Chem. Soc.*, 1912, xxxiv., 317.
3. Amos W. Peters, "Sources of Error and the Electrolytic Standardisation of the Conditions of the Iodine Method of Copper Analysis," *Journ. Am. Chem. Soc.*, 1912, xxxiv., 422; "A Critical Study of Sugar Analysis by Copper Reduction Methods," *Ibid.*, 1912, xxxiv., 928.
4. Leon Maquenne, "Estimation of Dextrose by Lehmann's Method," *Bull. Soc. Chim.*, 1898 (iii.), xix., 926; also *Journ. Chem. Soc. Abstr.*, 1899 (ii.), 529.
5. F. Lehmann, "A Volumetric Method for the Determination of Sugars," *Dissert.*, Marburg; through *Botan. Centr.*, 1910, xciii., 142.
6. F. M. Scales, "The Determination of Reducing Sugars—A Volumetric Method for Determining Cuprous Oxide without Removal from Fehling's Solution," *Journ. Biol. Chem.*, 1915, xxiii., 81.
7. L. S. Munson and P. H. Walker, "A Unification of Methods for Determining Reducing Sugars," *Journ. Am. Chem. Soc.*, 1906, xxviii., 663; P. H. Walker, *Ibid.*, 1907, xxix., 541; 1912, xxxiv., 202.
8. P. J. Cammidge, "An Improved Method for the Estimation of Sugar in the Urine and Blood," *Lancet*, 1917, cxciii., 613.
9. F. P. Treadwell, translated by W. T. Hall, "Analytical Chemistry," 1st Ed., cor. 1909, ii., 506.
10. Amos W. Peters, *Loc. cit.*
11. Should the colour at this point indicate lack of an

excess of copper, the test should be discarded and another experiment run, using less of the test solution.

12. This may be 10.00 cc. 0.1 N solution, 20.00 cc. 0.05 N solution, or 25.00 cc. 0.04 N solution. In blank tests or when the amount of reduced copper is seen to be small half this quantity of iodine may be used.

13. For most accurate results the thiosulphate solution should be run in in small quantities of 1.5 to 2 cc., shaking thoroughly after each addition, and running in the next portion while the liquid in the flasks is still in motion. See R. Kempt, *Zeit. Angew. Chem.*, 1917, xxx., 71; also *Chem. Abs.*, 1917, xi., 2646.

(To be continued).

ORDERS OF THE MINISTRY OF MUNITIONS.

AMMONIA AND AMMONIACAL PRODUCTS.

WITH reference to the Ammonia Control Order, 1918, dated May 17, 1918, the Minister of Munitions hereby orders as follows:—

1. The operation of the said Order is hereby suspended on and after March 14, 1919, until further notice.
2. Such suspension shall not affect the previous operation of the said Order or the validity of any action taken thereunder, or the liability to any penalty or punishment in respect of any contravention or failure to comply with the said Order prior to such suspension, or any proceeding or remedy in respect of such penalty or punishment.
3. This Order may be cited as the Ammonia and Ammoniacal Products (Suspension) Order, 1919.

POTASSIUM COMPOUNDS—KELP.

In reference to the Potassium Compounds Order, dated October 17, 1917, the Minister of Munitions hereby orders as follows:—

1. The operation of the said Order is hereby suspended on and after the date hereof (March 14, 1919) until further notice in so far as relates to Kelp.
2. Such suspension shall not affect the previous operation of the said Order or the validity of any action taken thereunder or the liability to any penalty or punishment in respect of any contravention or failure to comply with the said Order prior to such suspension or any proceeding or remedy in respect of such penalty or punishment.
3. This Order may be cited as the Potassium Compounds (Partial Suspension) Order, 1919.

BISMUTH ORES, BISMUTH METAL AND PRODUCTS THEREFROM.

In reference to the Bismuth Order, 1918, dated March 12, 1918, and the Bismuth (Amendment) Order, 1919, dated January 10, 1919, the Minister of Munitions hereby orders as follows:—

1. The operation of the said Orders is hereby suspended on and after the date hereof (March 14, 1919) until further notice.
2. Such suspension shall not affect the previous operation of the said Orders or either of them or the validity of any action taken thereunder or the liability to any penalty or punishment in respect of any contravention or failure to comply with the said Orders prior to such suspension or any proceeding or remedy in respect of such penalty or punishment.
3. This Order may be cited as The Bismuth Control (Suspension) Order, 1919.

National Association of Industrial Chemists.—A meeting will be held on Monday, March 31, at 8 p.m., at Burlington House, Piccadilly (by permission of the Chemical Society), when S. R. Todd, Esq. (Ministry of Labour) will speak on "Government Reconstruction Committees and Industrial Chemists."

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 6, 1919.

Dr. ALEXANDER SCOTT, M.A., F.R.S., Vice-President,
in the Chair.

It was announced that the Society had lost, through death, the following Fellows:—Norman Scott Rudolf, John Young.

Certificates of candidates were read for the first time in favour of Lionel Conrad Andrews, B.Sc., Cressingham House, Carshalton, Surrey; Nicholas Lionel Anfilogoff, Lathol House, Thames Haven, Essex; Edward Bloom, B.Sc., 61, Berwick Street, W. 1; William Brash, B.Sc., 53, Aynhoe Road, West Kensington, W. 14; Isaac Cohen, 50, Redmans Road, E. 1; Swondranath Dhar, 21, Cromwell Road, S. Kensington, S.W. 5; Ralph Eddowes Garrod, M.A., 5, College Gardens, Dulwich Village, S.E. 21; Edgar Thomas Griffiths, 100, Commercial Street, Tredgar, Mon.; Thomas Owen Griffiths, B.Sc., Hazelwood, Erskine Road, Colwyn Bay; Thomas Haigh, B.A., 15, Cavendish Avenue, Church End, Finchley, N. 3; Frederick Denison Maurice Hocking, 18, Woodside Park Road, N. Finchley, N. 12; George Hugh Hodgson, 41, Roach Road, Sheffield; Armand Houssa, B.Sc., 11, Tremadoc Road, Clapham S.W. 4; Henry Lawrence Long, B.Sc., 19, Seward Road, Hanwell, W. 7; William McHutchison, B.Sc., 108, City Road, Edgbaston, Birmingham; William Angus McIntyre, B.Sc., 18, Leinster Avenue, East Sheen, S.W. 14; John Alexander McNaughton, Birkwood, Redhill, Castleford; Samuel Mellins, 50, Great Garden Street, E. 1; Francis William Moorhouse, 57, Frodingham Road, Scunthorpe; Kishori Lal Moudgill, B.Sc., Christ's College, Cambridge; Hari Das Sen, M.Sc., Nawabganj, Cawnpore, India; Edmund Joseph Sterne, Felsham, Bury St. Edmunds; Donald Willoughby Capon West, Sleaford, Horsham, Sussex; Alfred Sydney Vince, 30, Ravensbourne Road, Catford, S.E. 6.

The following papers were read:—

"The Preparation of Monomethylamine from Chloropiricin." By P. F. FRANKLAND, F. CHALLENGER, and N. A. NICHOLLS.

"The Preparation of Monomethylaniline. By P. F. FRANKLAND, F. CHALLENGER, and N. A. NICHOLLS.

Ordinary Meeting, February 20, 1919.

Sir W. J. POPE, K.B.E., F.R.S., President,
in the Chair.

It was stated that the Society had lost, by death, the following Fellows:—Herbert Stoddard Coleman, George Carey Foster, Edward Lewis James, John Falconer King, George Martineau.

Certificates were read for the first time in favour of Robert Parmenter Burwell, B.Sc., 92, Southtown Road, Great Yarmouth; Charles Hall, Woodbridge School, Woodbridge; Vernon Percy Hart, 42, Park Grove, Portway, West Ham, E. 15; Sidney John Hopkins, London House, Hambledon, Hants; Fred Hughes, 39, Lord Street, Runcorn; Lazarus Mendel, 25, Broadway, West Ealing, W. 13; Rames Chandra Ray, M.Sc., Moradpur P.O., Bankipore, India; Nathan Singer, 147, Union Clapton Road, E. 5; William Arthur Walmsley, B.Sc., 17, Elmfield Road, Davenport, Stockport.

A certificate for election has been authorised by the Council for presentation to ballot under By-law 1. (3) in favour of Prof. Clarence Thomas Hamill, 606, Walnut Avenue, Syracuse, N.Y., U.S.A.

The President announced that the following changes in the Officers and Council were proposed by the Council: As Vice-Presidents to Retire—Prof. G. G. Henderson and Prof. A. Lapworth.

As Ordinary Members of Council to Retire—Mr. A. Chaston Chapman, Mr. D. L. Chapman, Sir Herbert Jackson, and Dr. F. L. Pyman.

As President—Sir James J. Dobbie.

As Vice-Presidents who have filled the Office of President—Prof. H. E. Armstrong, Prof. A. Crum Brown, Sir William Crookes, Sir James Dewar, Prof. Harold B. Dixon, Prof. Percy F. Frankland, Dr. A. G. Vernon Harcourt, Prof. W. Odling, Prof. W. H. Perkin, Sir William J. Pope, Prof. J. Emerson Reynolds, Dr. Alexander Scott, Sir Edward Thorpe, and Sir William A. Tilden.

As Treasurer—Dr. M. O. Forster.

As Secretaries—Dr. Samuel Smiles and Prof. J. C. Philip.

As Foreign Secretary—Lieut.-Col. Arthur Crossley.

As Vice-Presidents—Prof. F. G. Donnan, Dr. H. J. H. Fenton, Lieut.-Col. A. Smithells, Prof. James Walker, Prof. W. P. Wynne, and Prof. Sydney Young.

As New Ordinary Members of Council—Prof. F. E. Francis, Mr. J. A. Gardner, Dr. C. A. Keane, and Sir Robert Robertson.

Mr. C. F. Cross, Mr. A. R. Ling, and Dr. G. Senter were elected Auditors to audit the Society's Accounts.

Dr. A. Bramley and Mr. P. Edgerton were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared elected as Fellows:—Pierre Beghin; Walter Richard Berry, B.Sc.; Reginald Christopher Bickmore; Harry Blackman; Philip Blackman; Harold Samuel Bolton; Stanley Edward Bowrey, B.Sc.; Solomon Nathan Brown; John Joseph Bryant; Alan Chamley Burns, B.Sc.Tech.; George Butterworth; Harold Frank Cabell, B.Sc.; William Harold Squier Cheavin; John Arthur Clements; Edward Charles Cull, B.Sc.; Vishwanath Ganesh Dani, B.A.; Thomas Robert Dixon; John Campbell Earl; Percy Edwin Evans, M.A.; Alfred Farnbrough; James Darnell Granger, Ph.D.; Algie Hancock; Walter Arthur Nelson Hardwick; Benjamin Richard Heasman, B.Sc.; George Samuel Heaven, B.Sc.; James Rintoul Higham; Geoffrey Isherwood Higson, M.Sc.; Frederick William Hodkin, B.Sc.; Harry Jephcott, M.Sc.; André Job; Richard Edward Johnston; Edward Likiernik, B.Sc.; Francis Fredk. Mooney; Sydney Walter Morris; Charles Moureu; William Adrian Thomas Nash; Parnell Stanley O'Dowd; John Parrish, B.Sc.Tech.; Francis Falconer Peet, B.Sc.; Ernest Ed. Pendlebury; Frank Radcliffe, M.B., B.S.; Josslyn Vere Ramsden; Albert Riley, B.Sc.; Thomas John Samuel; Frank Comer Savage; Ernest Shepherd, B.Sc.; Arthur John Griffiths Smout; Edward Tyghe Sterne; Hugh Vernon Thompson, M.A.; Rupert Harry Tuelove, B.Sc.; Frederick Wilson Walker; Francis Henry Sweeting Warneford, B.Sc., B.A.; Walter Henry Watson, B.Sc.; Leo Daft Williams; Greatrex Johnson Woods; Charles Thomas Woosnam, M.A.

The following paper was read:—

"Nitro-, Arylazo-, and Amino glyoxalines." By R. G. FARGHER and F. L. PYMAN.

OBITUARY

PROF. EDWARD CHARLES PICKERING.

WE regret to announce that Prof. Edward Charles Pickering, Director of the Astronomical Observatory of Harvard College, died in Cambridge, U.S.A., on Feb. 3, in the seventy-third year of his age.

Prof. Pickering was born in Boston, and was educated at the Boston Latin School, and at the Lawrence Scientific School of Harvard, where he was afterwards appointed Instructor in Mathematics. In 1867 he became Thayer Professor of Physics at the Massachusetts Institute of Technology, and ten years later he was appointed Director of the Astronomical Observatory of Harvard

College. Prof. Pickering made a special study of stellar photometry, and was the inventor of the meridian photometer, with which an enormous number of measurements of the light from the stars has been made. Expeditions were sent, at Prof. Pickering's instigation, to various localities on the Andes to make a survey of the sky of the Southern Hemisphere, and finally a permanent branch of the Harvard Observatory was established at Arequipa. Under the directorship of Prof. Pickering the workers at Harvard Observatory have undertaken investigations which have led to important advances of astronomical knowledge, including the discovery of many new stars, of variable stars, and of binary stars whose nature is revealed only by spectroscopy, and the annals and other publications of the observatory, of which there are some 60 volumes, give an insight into the extraordinary comprehensiveness and thoroughness of his work. He was a D.Sc. of Victoria University, a Ph.D. of Heidelberg, and in 1907 was elected a Foreign Member of the Royal Society; he was the recipient of the Bruce, Draper, Rumford, and two gold medals of the Royal Astronomical Society.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxvii., No. 23, December 2, 1918; No. 24, December 9, 1918.

These numbers contain no chemical matter.

N^o. 25, December 16, 1918

Distribution of Mineral Elements and Nitrogen in Etiolated Plants.—G. André.—Haricot beans were grown in the dark, and the young plants were analysed as seeds as similar as possible to those which were allowed to germinate. When the distribution of mineral elements and nitrogen in the cotyledons, stems, &c., was studied, it was found that lime mostly remains in the cotyledons, while magnesia shows a greater tendency to pass into the young plant. Potassium shows the greatest power of migrating from the cotyledons, but the most remarkable relation which was established was the fact that three quarters of the nitrogen and phosphoric acid present in the seed were transferred from the cotyledons to the young plant in twenty-five days' growth in the dark. Sulphur behaved in the same way as phosphorus.

MISCELLANEOUS.

Purification of Gallium by Electrolysis and the Compressibility and Density of Gallium.—Theodore W. Richards and Sylvester Boyer.—Gallium occupies a place in the electrolytic series between indium and zinc, being far less easy to deposit than indium and much more easy than zinc. By carefully regulating the hydrogen ion concentration and current density gallium can be completely separated from indium electrolytically, and by this means a product having a higher melting-point than any previously known sample was obtained. The compressibility of gallium in both the solid and liquid states was determined. Gallium possesses the remarkable and rare property of occupying more volume in the solid than in the liquid condition. The compressibility of solid gallium places the element on the curve joining the other compressibilities in the graph representing the periodic relation of this property to atomic weight. Liquid gallium has almost exactly the same compressibility as mercury, and its value is nearly twice as that of solid gallium, although its volume is less. This confirms the universal experience that solids have compressibilities distinctly less

than the same substances as liquids, entirely irrespective of the volumes which they occupy. The most marked case of this kind so far observed is that of ice. It has been suggested that the expansion of gallium on freezing may be attributed to the presence of impurities, but the authors' experiments indicate that this is not the case.—*Journal Am. Chem. Soc.*, 1919, xli., 2, p. 133.

Radio-activity and the Coloration of Minerals.—Edgar Newbery, D.Sc., and Hartley Lupton, B.Sc.—The varied and brilliant coloration of many minerals has attracted the attention of many observers, but no generally accepted explanation has yet been put forward. The authors have undertaken an investigation of the part possibly played by radio-active substances in causing the exotic colours of certain minerals. The substances chosen for experiment were mostly clear crystals such as diamond, fluor spar, cryolite, quartz, selenite, anhydrite, apatite, tourmaline, calcite, &c., and the properties studied were colour changes on heating, and on treatment with radium or cathode rays, and luminescence in the same conditions. There appears to be little doubt that the colours and thermoluminescent properties of many minerals are due to the presence of radio-active matter, either in the water from which they have been deposited or by the action of radio-active minerals in their immediate vicinity. It appears possible that fluorescence is produced by α -radiation as in the case of zircons, while different colours may be produced by β and γ radiation, and all three effects may be observed in one and the same crystal. In nearly all cases the colours produced are due to the dissociation of minute traces of certain impurities. The products of dissociation are removed to a very short distance from each other, and the size or density of these particles will determine the particular colours of light absorbed or transmitted. When the molecular structure of the crystal is disturbed by heat, &c., the dissociated particles approach and recombine with consequent loss of colour. The emission of light on heating the radiated crystals is probably due to intense vibrations set up by the dissociated atoms coming together again. The impurities which give rise to this luminescence are frequently quite independent of those which produce the colour effects, since quite colourless crystals sometimes give brilliant thermo-luminescent effects, and deeply coloured crystals may give little or no visible luminescence during discharge of their colour. It appears to be fairly well established that phosphorescence cannot be produced in a perfectly pure substance, and the authors are of the opinion that thermo-luminescence, cathode-ray colours, exotic colours in minerals, &c., are due to the dissociation of traces of impurity in the bodies concerned and not to the decomposition of the body itself. The marked differences in the action of β and γ rays in producing different colours, thermo-luminescence, &c., in certain minerals seem to indicate some essential difference in the nature of these rays other than mere wave-length.—*Memoirs and Proceedings of the Manchester Literary and Philosophical Society*, lxii., Part III.

MEETINGS FOR THE WEEK.

- MONDAY, 24th.—Royal Society of Arts, 4.30. (Cantor Lectures). "Coal and its Conservation," by Prof. W. A. Bone.
TUESDAY, 25th.—Royal Institution, 3. "British Ethnology—The People of Scotland," by Prof. A. Keith.
WEDNESDAY, 26th.—Royal Society of Arts, 4.30. "British Engineering and Hydro electric Development—the Training of Engineers," by A. Hartley Gibson.
THURSDAY, 27th.—Royal Institution, 3. "Fire Cracks and the Forces producing them," by Prof. C. H. Lees.
— Royal Society, 4.30. "Genesis of Edema in Beri-beri," by R. McCarrison. "Morphology and Evolution of the Ambulacrum in the Echinoidea," by H. L. Hawkins.
FRIDAY, 28th.—Royal Institution, 5.30. "The Air Road," by Right Hon. Sir J. H. A. Macdonald.
SATURDAY, 29th.—Royal Institution, 3. "Spectrum Analysis and its Application to Atomic Structure," by Prof. Sir J. J. Thomson, O.M.

THE CHEMICAL NEWS

VOL. CXVIII., No. 3076.

ATOMIC STRUCTURE AND CHEMICAL AFFINITY.

By F. H. LORING.

ONE of the most fascinating problems in the whole domain of science is that of chemical affinity, which is at once of intense theoretical interest and of great practical importance. The problem must of necessity be approached by methods of analysis which are to some extent speculative, as the experimental evidence in this case is not such as to permit of extended developments without drawing tentative conclusions from closely related phenomena.

It is surprising, however, how much insight into the problem of chemical affinity can be obtained by a careful piecing together of known facts. Facts, which upon first consideration appear to be only remotely related to the subject in question, fit more connectedly into the scheme of matter as the examination is pressed in the direction leading to the electrical theory of the atom. The following notes are intended to bring the subject fairly up to date from the atomic point of view.

1. If the present theory of the electronic structure of the atom be accepted, in which case the electro-positive nucleus is the seat of the principal mass, this mass holding by mutual attraction electrons in orbital motion round its geometric centre, then a clue is afforded as to the system which enables atoms to unite in chemical bondage. The nucleus itself may represent a condensation of nuclei in proportion to its mass. The extent to which this theory has been developed will be seen from what follows.

2. It is obvious that the three states of matter, solid, liquid, and gaseous, profoundly modify the cohesiveness of substances, even to the extent of influencing the underlying chemical combinations present, so that few properties can be considered as *causes unto themselves*, so to speak. The properties of the atom should be considered from the point of view of their relation to other atoms, involving valency, affinity, cohesion, &c. Moreover, the atom should be considered from the other point of view, that of its component parts, as revealed by radio-activity and various phenomena brought to light by experimental research in the domain of molecular physics.

3. Radio-activity is an absolutely self-contained and self-centred phenomenon, since no influence which has been brought to bear on the process of atomic disintegration in any way modifies the activity. Similarly, in all chemical reactions the principal mass of the atom is unchangeable. These phenomena have their origin in, or belong to, the inner part of the atom; whereas, valency and other variable properties, including affinity and cohesion, are regarded as belonging to the outer part of the atomic system, and consequently suffer change when the environment alters. It is true that the radio-atoms change in valency when disintegration takes place, which action would seem to imply that valency is a property of the inner part of the atom. It is probable that some rearrangement of the outer electrons is brought about by the breaking up of that part of the atom which is stable up to the time of occurrence of the phenomenon.

4. Lord Kelvin attempted to explain cohesion by supposing that a substance was concentrated into element volumes quite small in comparison with their whole volume. The density at such centres was supposed, therefore, to be sufficient to make the inverse-square law of gravitational attraction applicable. Calculations based upon recent information, however, do not seem to confirm this view, for the distance between atoms in a steel bar would have to be of the order of 10^{-2} cm. (see H.

Chatley, *Phys. Soc. Proc.*, August, 1915) if gravitational attraction as expressed by the inverse square law was alone the cause of the cohesion.

5. Nagaoka (*Nature*, 1904, ix, p. 392) investigated mathematically a Saturnian type of atom, which would be stable if the centralised attractive force be large and the electrons be in rapid orbital motion. The *Æpinus* atom of Kelvin, consisting of electrons combined with a single positive particle of equivalent electrical charge and the electrons moving in circular orbits, would, according to Nagaoka (*Math. and Phys. Soc. Tokio*, 1905, ii., 20, p. 3161), give rise to an attraction or bondage between such atoms when the electrons of one orbital system come under the proper influence of another such system; that is to say, there is an attraction between each positive particle and the negative electrons common to both atoms. Since many molecules are diatomic the action of two atoms, instead of three or more, may be taken as characteristic.

6. In addition, there would be repulsions (1) between the sets of revolving electrons and (2) between the central charges which are of like sign. These actions would cause attractions (see 5) and repulsions that Nagaoka estimated would vary inversely as the fourth power of the distance between the atoms. When the atoms unite to form molecules the attraction will be jointly proportional to the respective masses, or proportional to the amount of positive or negative charges involved. The question of the stability of such an atom has been in dispute, and to overcome this difficulty a sufficiently strong central charge has been postulated.

7. Sir J. J. Thomson (*Phil. Mag.*, March, 1914, vii., p. 237) developed in detail a type of atom in which the electrons were in orbital motion in a sphere of uniform positive electrification, the electrons being considered for convenience of calculation to be arranged in concentric rings. The stability of the system would be upset when the electrons fall below a critical speed, resulting in an atomic convulsion and a rearrangement of the electrons, some of which would be expelled from the system, thus, in a measure accounting for the disintegration of certain radio-elements. Under normal conditions such a system would have the merit of stability.

8. It was shown that the electrons might revolve in stable rings, concentrically disposed, and by determining a series of stable combinations involving different numbers of electrons, Sir J. J. Thomson was able to present a scheme which simulated the periodic table of the elements in that successive evaluations of recurring types of atoms were shown in terms of such rings. Different arrangements of electrons were supposed to give rise to varying degrees of stability, but cases were shown, for example, in which a ring may acquire one or two extra electrons and yet remain stable, whilst other rings may part with an electron without losing their stability, the former representing the *electro-negative atom* and the latter the *electro-positive atom*.

9. The possibility of electro-magnetic radiations being emitted by electrons in rapid orbital motion had to be considered, since any appreciable loss of energy would result in the slowing down of the electrons, and, in consequence, the disturbance would give rise to the ejection of electrons from the atom as in radio-cative phenomena.

10. Sir J. J. Thomson showed, however, that the radiant energy from a ring of electrons in rapid orbital movement diminishes rapidly with the number of electrons in the ring. For example, increasing the number of electrons from 1 to 10 decreases the radiation to 10^{-5} the original value, if the particles are moving in both cases with $1/10$ the velocity of light. By decreasing the velocity to $1/100$ that of light, the radiation still further diminishes, so that it becomes 10^{-16} of a single electron moving with the same velocity. Whilst this action might apply to the disintegration of the radio-atom, it does not explain the absence of radio-activity amongst those elements supposed to have only a few electrons unless a relatively low angular velocity be assumed.

11. Later, Sir J. J. Thomson (*Phil. Mag.*, 1906, xi., p. 769) concluded from several lines of argument that the number of electrons in the atom was about three times its atomic mass (atomic weight). Since the mass of the electron is about 1/1700 that of the hydrogen atom, a large part of the atomic mass must be composed of something different from the electrons. Matter may be wholly "electric" if the counterpart to negative electricity (electrons) is matter itself, but conferring on matter the electric title does not in this case mean that it is endowed with the characteristics belonging to the electron. The duality may comprise matter pure and simple on the one hand and negative electrons on the other (see 19).

12. Dr. N. Bohr's theoretical work on the Rutherford atom (thus designated owing to Rutherford's classical researches in radio physics and his views of the atom—see 29) are of particular interest (see latest paper, *Phil. Mag.*, 1915, xxx., p. 394). Dr. Bohr took a very advanced step in abandoning ordinary mechanics or electro-dynamics when studying the atom as a radiator of energy which is systematically revealed by the spectroscopy, and he based his mathematical treatment of the atomic system on Planck's famous quantum theory, the outcome being a system which possesses a number of states when no emission of radiant energy takes place, even if there be relative movement amongst the particles, and these states themselves do not lead to any conflict with mechanical principles or electro-dynamical theory; but, on the other hand, according to the theory, there are active states when radiation of energy takes place, the quantum idea being applicable. The energy radiation is therefore supposed to take place in jumps or quanta between non-radiant states, the emitted radiation at each stage being homogeneous, and the frequency (ν) multiplied by Planck's constant (h) gives the energy (A). Thus, $h\nu = A_1 - A_2$, where A_1 and A_2 are the respective energies of the system in two non-radiant states. The various states of a system comprising an electron rotating round a positive nucleus is determined by the relation: Mean value of the kinetic energy of the system = $\frac{1}{2}nh\nu$, where ν is the frequency of rotation of the electron round the nucleus and n a whole number. These relations have led (1) to an interpretation of the Balmer formula for the spectrum of hydrogen, and (2) to a determination of the Rydberg constant.

13. A. van den Broek (see *Nature*, 1913, xcii., p. 372 and p. 476; also Soddy, the same, p. 399 and p. 452; also Rutherford, the same, p. 423) suggested that the positive charge instead of being a definite fraction of the total atomic mass (see 11) might coincide with a number corresponding with the place of the element in the Mendeléeff periodic table when the elements are numbered consecutively, beginning with hydrogen No. 1, helium No. 2, and so on up to uranium now known to be No. 92. Interpreted in a physical sense this may mean that the atoms are built up with positive charges and corresponding electrons in a regular manner.

14. The late Dr. H. G. J. Moseley (*Phil. Mag.*, 1913, p. 1024, and 1914, p. 703) directed a pencil of cathode rays (electrons) against elementary substances arranged in each experiment as an anti-cathode in a vacuum tube, using a crystal of potassium ferrocyanide as an analyser, the elements being studied in the order of their atomic masses. Moseley found, upon the analysis of the X-rays excited by this bombardment and recorded photographically, that two strong lines, designated α and β , were of wavelengths inversely proportional to $A(N-b)^2$, where N is the atomic number and A and b are constants. A simple numerical relation was thus shown, apparently establishing the significance of the atomic numbers (see 13).

15. The periodic table of the elements is anomalous in respect of argon-potassium, cobalt-nickel, and tellurium-iodine, these elements being in the wrong order to be in chemical harmony with their homologues; i.e., when the foregoing elements are arranged in the order of their respective atomic masses. The atomic numbers, however, give these elements their correct chemical positions, so

that the discovery of Moseley supports the idea that the electrical characteristic of the atom transcends the mass value (atomic weight) in respect of fundamental importance, or that the properties of the elements are due to electrical combinations rather than mechanical ones. Moreover, the X-ray analysis predicts elements for the gaps in the periodic table between molybdenum and ruthenium, neodymium and samarium, tungsten and osmium; and when the principle is extended to the radioactive products those of chemical identity and inseparable by chemical means, though differing in atomic mass, have the same atomic number, the last-named type of elements being called *isotopes* (see 23).

16. Returning to the relation discovered by Moseley, there are two principal series of lines, K and L, resulting from the bombardment of the elements, there being two strong lines as indicated above (14). In the case of those elements of lower atomic mass, they exhibit a number of faint lines in addition. In the L series, which has been examined for the elements from zirconium upwards, there are usually five well-marked lines, namely, α , β , γ , δ , and ϵ , which decrease in intensity and wave-length from α to ϵ . Other faint lines are also present.

17. Prof. O. W. Richardson ("Electron Theory of Matter," 1914, p. 511) refers to Moseley's relation in the following terms: "The frequencies of ν of each sub-series are determined by the equation—

$$\nu = A(N-b)^2,$$

where A and b are constants characteristic of each sub-series. For the lines denoted by a in the K series—

$$A = \left(\frac{1}{1^2} - \frac{1}{2^2} \right) \nu_0 \text{ and } b = 1,$$

and for the lines denoted by a in the L series—

$$A = \left(\frac{1}{2^2} - \frac{1}{3^2} \right) \nu_0 \text{ and } b = 7 \cdot 4.$$

In the above ν_0 is the fundamental Rydberg frequency in the formulae for the optical spectra of the elements. For the K series the agreement is quite exact, but in the L series there is a slight deviation from linearity with the elements of very high atomic weight" (see 12).

18. The chemical properties of the elements are thus determined by the atomic numbers when they are substituted for the atomic masses; or, to state this rule another way and comment thereon, the atomic masses of the elements are not quite regular enough in some cases to enable all the elements to be accurately placed in the periodic table, but by employing atomic numbers the periodic law is accurately fulfilled subject to two reservations: in respect of (1) the rare-earth elements and (2) those of Group VIII. in the table. The rare-earth elements do not exhibit the same characteristic change in chemical properties (e.g., valency), as is the case with regard to other elements of higher and lower atomic mass in passing from member to member across the table; yet the atomic numbers seem to assign these elements to successive places in the table. Similarly, the elements of Group VIII., though bearing consecutive atomic numbers, are closely allied in chemical and physical properties. These difficulties from a classification point of view may be removed by grouping such elements in branch systems. The radio-elements also may be regarded collectively as a branch or extended system, though, from the group or valency point of view, there is a characteristic change in passing from member to member as in the normal part of the table.

19. The famous Prout hypothesis (1815-16), that all the elements are made up of hydrogen taken as a primal unit, hydrogen thus becoming a sub-atom, has grown in favour lately. The prevalence of electrons in, or associated with, all atoms and their definitely observed occurrence as ejectamenta along with helium atoms in the spontaneous breaking down of certain very massive atoms (radio-atoms) situated at the extreme end of the periodic table, points

to the principle of two common constituents for all atoms. It is only a step to consider the positive counterpart to the negative electron as the stuff out of which the mass of the hydrogen unit is made; but with this difference as a further consideration, that the positiveness is probably a fundamental attribute of matter distinct from electronic activity. The following statement by Prof. Soddy in *Engineering*, of May 25, 1917, being taken from a report of his discourse to the Royal Institution, is of interest in this connection:—

"The confusion between the earlier and present views concerning the relations between matter and electricity," Prof. Soddy continued, "was a further obstacle to the student. We knew negative electricity apart from matter as the electron; we knew positive electricity, apart from the electron, the hydrogen atom or the α particle (helium atom), and that was matter in the electrically uncombined condition. Whether we spoke of positive and negative electricity, or matter and electricity, the dualism remained. On the other hand, the theory of electro-magnetic inertia was true monism; it tried to explain two things, the inertia of the electron and the inertia of matter, by the same cause. There was no reason to assume that matter minus its electron was made of the same stuff as the electron itself."

20. The following taken from an article of mine (*CHEMICAL NEWS*, Oct. 11, 1918, cxviii., p. 319) deals with the problem of valency and cohesion from an elementary point of view:—

Radio-active phenomena indicate that possibly helium is a common constituent of all atoms except hydrogen, in which case its combination must be of a superior order to anything coming within the range of controllable phenomena known as chemical action, but like the molecule in crystals (see below) the definite individuality of such a fundamental helium atom or unit taken as a sub-atom may be lost, or merged into a larger whole. In this case a deep-seated type of valency may exist accompanied with an affinity far superior to anything exhibited in chemical phenomena, just as ordinary valency is in a sense more fundamental and definite than that which is connected with the formation of molecular complexes. The gradation is fairly complete as the last mentioned phenomenon shade off into cohesion. It will be seen that this line of reasoning leads to four physico-chemical steps, namely:—

1. Helium atoms as sub-atomic units, involving a superior type of valency and affinity. A further sub-division into similar hydrogen units has been foreshadowed as a possibility, in which case a similar antecedent step to this one might be expected.
2. Atomic combinations under control of the chemist, involving ordinary valency, but with affinities which are not co-related to the valency values.
3. Molecular complexes, involving a sort of residual or excess valency which tends to become diffuse.
4. Cohesion, involving a still more remote type of valency which being wholly diffuse is more of the nature of an affinity pure and simple, and, indeed, in this case the idea of *valency* may be entirely eliminated.

It is to be noted in connection with the above statements that null-valency and zero chemical affinity coincide in the case of the inert gases of Group 0, but in respect of the elements of other groups there is no rule co-ordinating valency and chemical affinity.

21. The idea of considering hydrogen as an electro-positive unit in the structure of the atom, is attended with several difficulties. In the first place 16 hydrogens ($H = 1.008$) as sub-atoms would not yield oxygen of atomic mass 16 exactly, but there is no need of considering for the present a unit differing from absolute unity in value. In the second place there is a real difficulty in cases where

the built-up atom has a fractional mass value of considerable magnitude as, for example, chlorine 35.45, and silver 107.88; but in these cases the discovery of isotopes seems to come to the rescue, although judgment must be suspended pending the actual experimental confirmation that there are isotopic atoms in the composition of elementary mass aggregates of this type. Some physicists have reason to doubt the existence of isotopes except in the case of lead and the radio-active elements. The positive-ray experiments of Sir J. J. Thomson do not appear to have quite definitely settled this point (see "Rays of Positive Electricity," by Sir J. J. Thomson). Sir William Crookes suggested many years ago that the individual atoms may not be exactly alike in mass, and consequently the measured values may be average figures.

22. Sir J. J. Thomson and Sir E. Rutherford have considered the possibility of a change or disappearance of some of the mass when the sub-atoms united or polymerised to form the suggested atom of n units mass, so that, for example, $H = 1.008$ taken 16 times is 16 exactly. To account for this violation of the principle of the conservation of mass, the masses involved have to be treated as wholly of electro-magnetic origin (as in the case of the electron), and when combined the fields are supposed to have interacted so as to give the result required. Sir J. J. Thomson, in discussing the problem from an energy point of view apart from that of isotopes, suggested that in this action an enormous amount of energy would be involved (see Thomson, "Atomic Theory," Romanes Lecture, 1914), especially in the case of the formation of the part of the chlorine atom represented by the decimal fraction (0.45).

23. The radio-elements, however, offer a clue to the possible solution of this difficulty. Amongst these elements there are atoms differing by several whole-number units in their mass values, yet so chemically and spectroscopically alike that no separation or distinction can be made, and it is only by the process of radio-active change from one element into another that this fact was discovered. Prof. Soddy has made a special study of this phase of radio-activity and he has designated such elements *isotopes*. Lead from different sources has been found to possess different atomic masses. This element is now regarded as the end-product from two or three lines of atomic disintegration, at least in certain cases; hence the difference in atomic mass. Since some lead is the end-product of a process of *devolution*, there may be also some lead that is the end product of *evolution*, the two processes culminating at one place in the periodic table, the former process being retrograde in character.

24. A study of the periodic table reveals the fact that it is made up entirely of elements approximating to isotopes. For example, lithium, sodium, and potassium are very nearly alike chemically, though spectroscopically quite distinguishable. They occupy a one-group place in the table. These elements differ from each other in atomic mass by 16 units, and there are other instances in which the difference is greater. The radio elements, on the other hand, are of much higher atomic mass, and the differences in respect of the isotopes are, relatively to the total masses, considerably less. It is not therefore so surprising that certain radio-atoms should be identical chemically and spectroscopically. In the instance of lead, which has a high atomic mass (207) a variation of several units would not be expected to give an appreciable chemical and spectroscopic difference; that is to say, so long as the atoms under consideration are of the same group. This idea tells against extending the scheme of isotopes to the elements of low atomic mass; but, here again, a curious circumstance seems to obviate in a measure at least the difficulty under discussion.

25. The very low atomic-mass elements are practically whole numbers; i.e., without fractions of appreciable magnitude. Beginning with hydrogen, the first departure involving a large fraction (neglecting Be 9.1) is that of magnesium 24.32. The two neons (mean value, 20.2)

distinguished by Sir J. J. Thomson by means of positive-ray analysis, strengthens the idea of extending the isotopic principle to explain fractional irregularities amongst those elements whose atomic masses are known to be fairly accurately determined. The neons in question have values 20 and 22, but since these are relatively fewer atoms present of the higher value, the mean, 20.2 (determined by density measurements), is to be expected. The atomic mass of silver is very accurately known, whilst the values of copper and gold are known with considerable accuracy. The following scheme (see a note of mine, *CHEMICAL NEWS*, 1914, cix., 143) represents a guess at possible isotopes, but this method must not be taken as anything more than an illustration of the idea of extending the principle in question to non-radio-active elements. The whole numbers are, of course, arbitrary as they have not been arrived at by experiment.

Copper.	Silver.	Gold.
$63 \times 7 = 441$	$107 \times 7 = 749$	$196 \times 7 = 1372$
$(63+4) \times 1 = 67$	$(107+4) \times 2 = 222$	$(196+4) \times 3 = 600$
8) 508	9) 971	10) 1972
63 50	107 88	197.2
Exp. values 63 57	107.83	197.2

It is just possible that the masses of the isotopes of the non-radio-active elements have become equalised by some process of interchange of energy, so that schemes such as here shown cannot be tested by experiment. Some advanced physicists regard all mass as purely a manifestation of confined energy. (See "Electron Theory of Matter," by O. W. Richardson, p. 318).

26. In considering the Prout hypothesis (see 13) the question might be raised as to whether the sub-atomic units give rise to a nuclear or central mass varying in diameter proportionately to the number of such units co-ordinated in the atom. The positiveness of the atoms in Group I. of the periodic table varies from lithium to caesium, the latter being probably the most electro-positive element known. This might be accounted for if the diameter of the atomic nucleus is constant, whilst the density varies in proportion to the number of positive sub-atomic units contained therein. The presence of electrons in the atom conditions the electro-positive effect, however, and this must be taken into account. For example, caesium contains more electrons than lithium, which is of low atomic mass, and the electro-positiveness of the nucleus of the caesium atom may itself be even greater than that indicated chemically, or by the position of this element in the electro-chemical series. Probably the electrons change their position by orbital orientation or otherwise, as is evidently the case in certain magnetic phenomena, and thereby the property in question is altered. It will be remembered that radium after losing a helium atom (the actual emission is α - and β particles) becomes an emanation (inert gas) with no chemical activity.

27. Prof. T. W. Richards has investigated the compressibility of the elements. The following table gives the compressibilities of a few elements in megabar units—each value to be multiplied by 10^{-6} —

Cæsium	61.0
Sodium	15.6
Lead	2.2
Aluminium	1.3
Red phosphorus	9.0
White phosphorus	20.3

It is to be noted that there is a large relative difference between the two varieties of phosphorus which seem to indicate that compressibility is a property distinct from any nuclear magnitude which is removed from the external regions of the atom.

28. Prof. Richards (*Am. Chem. Soc. Journ.*, Dec., 1914, xxxvi., 2417) assumes that the volume of the atom

is compressible as suggested by the variation of b in van der Waals' equation, but unlike this variable he assumes that the molecular bulk when not compressed may be about equal to the critical volume, but that this volume is already diminished by compression due to cohesion when the gas liquefies. The small compressibility of liquids and solids and the absence of appreciable contraction on cooling, points also to the close packing of the atoms.

The alkali metals suffer the following compressions and contractions:—

	Li.	Na.	K.	Kb.	Cs.
Compressibility ..	9.0	15.6	31.7	40.0	61.0
Contraction ..	17.6	21.5	33.1	36.8	53.6

The increase in contraction in passing from lithium to caesium is attributed to the increased compressibility of the metals with the larger atomic volumes.

29. Sir E. Rutherford has investigated the internal or sub-atomic structure of matter by studying the scattering of high-speed α and β particles in their passage through thin films. It was found that a small percentage of the total α particles suffered a deflection through an angle greater than 90° , and it was considered that such deflections could only be due to the particle passing very close to a single atom in its passage through the film. To account for this phenomenon, the atom of the film was supposed to possess a charge of positive electricity concentrated in a very small relative space in its centre. It was therefore "necessary to suppose that the greater part of the mass of the atom was associated with the positive charge which for distances up to 3×10^{-12} cm. behaved as if it were concentrated at a point" (Rutherford). The large angle of scattering was attributed to the intense electric field surrounding the centralised charge, and the laws of scattering have been experimentally verified by Geiger and Marsden, who found that the number of particles scattered, and the angle observed, fulfilled the theoretical requirements within the limits of experimental error over an enormous experimental range.

30. Moreover, the comparison of the experimental results with the electrical theory of the atom indicates that the central charge in the atom is about half the atomic mass, which is roughly the atomic number indicated by the experiments of Moseley (see above). The theory of scattering, however, requires a modification when the mass of the scattering atom approaches to that of the α particle which is the helium atom of atomic mass 4. The electrons are supposed to be distributed throughout a spherical volume or in concentric rings in one plane.

31. Sir E. Rutherford ("Radio-active Substances and their Radiations," 1913, 630) says:—"On this theory the α particle in rapid motion consists of two unit positive charges concentrated throughout a volume minute compared with the volume of the atom as ordinarily understood. Since it does not seem possible that the α particle can retain any of its constituent electrons in escaping from the radio-active atom and in its violent encounters with the atoms of matter it traverses in its path, it is reasonable to suppose that the neutral helium atom contains two unit positive charges and two negative electrons."

32. Prof. J. Perrin in his book "Atoms," 1916, 162, draws attention to the possibility that in the process of chemical dissociation the change is brought about by the action of electro-magnetic radiation. The rate of dissociation at constant temperature when a molecule A breaks up into its generators, taking a unit volume, is proportional to the concentration of the gas A, and the process cannot be altered by the admixture of other non-reacting gases functioning as dilutants. If the process depended upon the number of impacts, accepting the kinetic theory of gases, which is firmly established, the foregoing statement according to Perrin would not be an accurate rendering of fact, consequently he suggests that the underlying cause of dissociation is to be sought in radiant energy, since the rate of dissociation depends upon temperature inde-

pends of dilution, disregarding any catalytic action as ordinarily understood.

33. In connection with the foregoing statement the following radiations in wave-lengths from Dr. G. W. C. Kaye's book, "X-Rays," 1918, 234, may be of interest:—

Kind of wave.	Wave-length in cms.	
Hertzian waves ..	10^{-6}	to 0.2
Infra-red rays ..	0.031	" 7.7×10^{-5}
Visible light rays ..	7.7×10^{-5}	" 3.6×10^{-5}
Ultra-violet rays ..	3.6×10^{-5}	" 5.0×10^{-6}
X-rays ..	1.2×10^{-7}	" 1.7×10^{-9}
γ -rays ..	1.4×10^{-8}	" 1.0×10^{-10}

The ionising power of X-rays on gases and a weaker effect by ultra-violet rays should be noted.

34. Since β and γ rays are given out when atomic disintegrations take place (radio-activity) it is probable that radiant energy was absorbed when the atoms were formed. The type and intensity of these rays emitted varies amongst the radio-atoms and there are a few cases of rayless changes, as if β - and γ -rays were absorbed within the atom. There may be cases, however, in which the rays are expelled too slowly to be detected.

35. There is another class of phenomena that should be considered, and that is the part played by catalysts. The theory of catalytic or contact action has been expounded by chemists at some length and various views are held. One view is that a catalyst is a body which forms a transient compound with a reacting substance with which it comes into contact; but, that the compound so formed being itself unstable under the circumstances reverts in part, say, to its generators and the catalyst remains unchanged. Meantime, the compound temporarily formed gives rise to a "nascent" or active body which starts the proper action. The process repeats and extends. The reaction is delicately poised, consequently, a small amount of impurity, if of a certain kind, impedes or stops entirely the process, in which case it renders the catalyst incapable of taking part in the activity, somewhat in the same way that grease will prevent iron from rusting. Assuming, for example, that a substance de-oxidised as fast as it oxidised, it would remain unchanged, yet give rise to nascent oxygen, but if the substance is greased it would not oxidise even transiently. This statement is not intended to be more than a hypothetical case, by way of illustration. E. Jobling ("Catalysis and its Industrial Applications," 1916, p. 73) says, referring to methods of hydrogenation, "The mechanism of these remarkable reductions can be explained in several ways. It may be that the passage of the hydrogen over the finely-divided metal induces its decomposition into the atomic or 'nascent' state, or that the temporary occlusion of the hydrogen upon the catalyst favours its interaction with the reducible body. A more probable explanation is that put forward by Sabatier himself, who supposes the formation of an intermediate unstable hydride upon the surface of the metallic catalyst, this hydride being capable of furnishing its hydrogen rapidly and in a suitable state to a substance which is able to utilise it. There might even be a series of hydrides formed, in which case the varying degree of activity of the different metallic catalysts would be explained, since then the most powerful catalyst would be capable of forming the greatest number of hydrides."

36. I. Langmuir has investigated the adsorption of gases on plane surfaces of glass, mica, and platinum (*Am. Chem. Soc. Journ.*, Sept., 1918, xl., 1361), and he regards the adsorption in these cases to be due to chemical forces of the primary and secondary valence types, particularly the former in the case of metals. At low temperatures (-183° and -118° C.) relatively large amounts of gas are adsorbed by glass and mica except when hydrogen is used. With platinum, however, no adsorption could be observed even at -183° C. until after this metal had been heated to 300° C. in a mixture of hydrogen and oxygen, when "activation" took place, so that when oxygen was

brought into contact with CO adsorbed on the activated platinum CO_2 was formed, which at room temperature showed no tendency to be adsorbed by this metal.

37. In the analysis of crystals by means of X-rays, it has been found that the structure of the entire crystal is like one vast molecule, since the molecular identities, as exhibited when the substance is in a liquid or gaseous state, have more or less disappeared (see 20). This fact leads to two possible views in connection with (1) fundamental chemical combinations (sub-atomic phenomena) and (2) the action of a catalyst. In considering (1) the building up of the atoms from lithium to uranium by polymerisation of primal units, hydrogen and helium of atomic mass, respectively, 1 and 4, the idea of the nuclear part of the atom behaving like a crystal in having the original components merged as a whole, and the electrons present co-ordinated so as to form one orbital system, suggests itself. Such a system may, however, be of complex structure. It is a well-known fact that radio-active phenomena strongly supports the idea of a built-up atom owing to the reverse process revealed by atomic disintegrations. With regard to the possibility of (2), the action of the catalyst on molecular aggregates, i.e., atomic groups so bound together as to function as a unit molecule, the combination may take place in a small fraction of the whole mass, when started by the presence of a catalyst exposing "nascent surfaces" (if such an expression may be used) to reaction with the reacting substance itself, whereby the electrons take up new positions. There is here a suggestive parallel in the action of certain radio-atoms which change their chemical character without emitting rays of any kind (see 34).

It is unfortunate that such terms as *nascent* and *activated* are necessary, since these expressions do not advance the state of knowledge sufficiently to be of much use. It will be seen, however, that, as in all chemical actions, an electronic activity is implied, and when the mechanism of this activity is understood probably a definite meaning can be attached to these terms and chemical affinity in particular elucidated.

THE CASE FOR A RING ELECTRON.*

By Dr. H. S. ALLEN.
(Concluded from p. 139).

10. *The Zeeman Effect.*—In the simple theoretical explanation of the Zeeman effect first given by Lorentz, the motions of the electrons in a luminous source are analysed into three components, a vibration parallel to the lines of magnetic force and two circular motions, clockwise or anti-clockwise, in planes normal to the lines of force. The vibrations are assumed to take place under the influence of "elastic" forces, attracting the electrons towards a position of equilibrium. Although explanations of the magnetic effect have been given by the combination of the quantum hypothesis with Bohr's atomic model, Debye has emphasised the fact that with these assumptions there is no place left for the quasi-elastic oscillating electrons which have been used in all theories for the explanation of the Zeeman effect from Lorentz to Voigt. Mention should be made of the theory of Ritz in which the electron moves in an orbit in a plane perpendicular to the axis of a magnet formed by the addition of a number of elementary magnets, which are the same for all substances.

If radiation is due to pulsations in a ring electron it would seem that the Zeeman effect should follow from reasoning similar to that first employed by Lorentz.

For consider a "pulse" in the form of a small "hump" travelling round the ring. This may be regarded as

* Opening Paper on a Discussion on "The Case for a Ring Electron," at the Imperial College of Science, October 25, 1918. From the *Proceedings of the Physical Society*, xxxi., Part 2.

equivalent to a particle of mass km and charge ke (where k is a fraction of the total mass or total charge) travelling in a circular path under the influence of elastic forces. A magnetic field would produce a change of period (positive or negative) as in the theory of Lorentz proportional to ke/km , that is to e/m .

The complex resolutions sometimes observed under the influence of the magnetic field may possibly be explained as arising from more complicated pulsations of the ring. Runge has made known a rule which states that the complicated magnetic resolutions are in simple relation with the normal value of e/m . Ritz has endeavoured to explain the magnetic resolutions by a kind of precessional movement of the system round the lines of force as axis. This theory and those put forward by Lorentz and Voigt may be found discussed in the last chapter of Zeeman's "Researches in Magneto-optics." "Voigt has abandoned the supposition of magnetically isotropic arbitrarily orientated particles, and modified Lorentz's system of equations. He supposes that the radiating particles are orientated under the action of the field." The results obtained on this assumption are competent to explain all the resolutions observed. The hypothesis of the ring electron appears to furnish exactly what is required for a basis of this theory. In particular it explains the difficulty as to the absence of an undisplaced line in light emitted perpendicular to the field, for the electron would set at right angles to the magnetic field, and there would be no motion of parts of the ring parallel to the lines of magnetic force.

11. *Solar Electron Streams.*—The view that magnetic storms and the aurora are due to ionisation of the outer regions of the atmosphere by streams of electrons or ions projected from the sun is now commonly received. Schuster has drawn attention to the fact that the electrostatic forces due to a cloud of charged particles would tend to scatter the particles to a considerable extent (*Proc. Roy. Soc.*, 1911, lxxv., 44). If, however, the electron possesses the properties of a small magnet a little consideration will show that the magnetic forces would tend to diminish the scattering effect. This may make it easier to understand the sudden commencement of magnetic storms, which would be difficult to explain if the electron stream is widely scattered before reaching the earth. Even if the effect referred to is small it may not be negligible in the case of a crowd of electrons moving in a magnetic field.

12. *Chemical Considerations.*—Serious difficulties are met with when an attempt is made to apply the conception of the electron at present in vogue to problems of chemical constitution and stereo chemistry. Any theory in which the electrons are in rapid orbital motion is difficult to reconcile with the stereo-chemical evidence for a definite spatial arrangement of the groups of atoms attached to a carbon atom, especially as the rings of electrons must usually all rotate about the same axis. These difficulties have been discussed at length by Parson. What seems to be required is the existence of chemical "linkages" or "bonds" having definite relations in space with reference to the atom, and yet admitting of a certain mobility. This involves the presence of valence electrons which are at rest, or vibrating within narrow limits, near the surface of the atom. Stark has developed a theory on these lines, taking into consideration only electrostatic forces. Nicholson (*Proc. Phys. Soc.*, 1918, xxx., 65) has discussed the stability of such systems, and has shown that Stark's conclusions do not survive a quantitative treatment. It appears to be impossible for two atoms in a molecule to be linked by a single electron, or by two electrons, which attract both atoms.

The introduction of a magnetic electron, producing both an electric and a magnetic field, furnishes a means of avoiding these difficulties, so that it becomes possible to retain stationary electrons and at the same time the orbital motion which is required to explain radiation and magnetism. It is perhaps well to emphasise the fact that this

theory includes both electrostatic and magnetic attractions and repulsions. It is probable that the electrostatic forces play the most important part in the formation of chemical compounds, especially in those of "polar" type, whilst the magnetic forces may be regarded as permitting a stable arrangement of stationary atoms and electrons.

The presence of eight groups in the periodic table indicates that for the majority of elements eight electrons are required to form a stable system. This is brought out in the arrangement of the table which I published recently in the *Transactions of the Chemical Society* (1918, cxiii., 389). In place of Newland's "law of octaves" we have what may be termed the "rule of eight." This rule is brought into prominence when atomic numbers are inserted in the periodic classification.

The same rule is obeyed in the case of chemical compounds, as is shown most clearly by the "molecular numbers" which I have introduced. The molecular number signifies the sum of the positive charges carried by the atomic nuclei contained in the molecule. Both Parson and Lewis (*Journ. Am. Chem. Soc.*, 1916, xxxviii., 762) have emphasised the fact that the groupings required by chemistry are, in general, of two sorts, one a pair of electrons closely associated, and the other a very compact group of eight. These are exactly the groupings that might be expected from magnetic doublets, for Parson has shown that the group of eight forms an extremely stable system of low magnetic energy.

13. *Cohesion.*—That the cohesion of a solid arises from the action of electric or electro-magnetic forces may be inferred from optical experiments. The Lorentz-Fitzgerald hypothesis explains the negative result of the Michelson-Morley experiment by a contraction of the material framework of the apparatus in the direction of its motion through the æther. Such a contraction, which is essential according to the principle of relativity, may be predicted from the standpoint of electro-magnetic theory. There is therefore a strong presumption that the forces of cohesion between the particles which give a solid its rigidity are either electric or magnetic forces.

All chemical forces also are probably of electro-magnetic origin, and in the light of our present knowledge it does not seem possible or advisable to distinguish sharply between chemical and physical forces. Indeed, Langmuir (*Journ. Am. Chem. Soc.*, 1916, xxxviii., 2221), in an interesting paper on the constitution and fundamental properties of solids and liquids, concludes that both solids and liquids consist of atoms held together entirely by chemical forces. The phraseology may serve a useful purpose if it serve to emphasise the essential identity between the forces imparting rigidity of a crystal and those conferring stability on the molecule of an organic compound.

In this connection it is of interest to recall the work of Lewis (*Phil. Mag.*, 1914, xxviii., 104) on the relation between the internal pressure or cohesion P in the equation—

$$(p + P)(v - b) = RT,$$

and the dielectric capacity and magnetic permeability of a liquid. He has shown that the Obach-Walden relation regarding the proportionality between the internal pressure and the dielectric constant follows from the hypothesis that molecular attraction is electro-magnetic, not electrostatic in nature.

PART II.—THE PROPERTIES OF THE RING ELECTRON.

The Mass of the Electron.

The electron was originally regarded as a sphere or spheroid, and in this case the electro-magnetic mass may be calculated as was first shown by J. J. Thomson. The electro-magnetic inertia for the slowly moving sphere, charge e , radius a , is $2e^2/3ac^2$, where c is the velocity of light (see Schott, "Electro-magnetic Radiation," Appendices C and D). For the Lorentz electron, for which the shape alters as the acceleration proceeds, the longitudinal and transverse masses are equal to—

$$2e^2/3ac^2(1 - \beta^2)^{-3/2} \text{ and } 2e^2/3ac^2(1 - \beta^2)^{-1/2}$$

(where k denotes the ratio of speed of the centre to that of light), as required by the Principle of Relativity (Schott, *Proc. Roy. Soc.*, 1918, xciv., 422).

The question of the electro-magnetic mass of the ring electron has been discussed by Webster (*Phys. Rev.*, 1917, ix., 484), who has shown that the relativity principle requires certain assumptions about the internal energy, which, when made in the most plausible way, lead to the result that the mass of the electron is $2/c^2$ times its electrostatic energy. In ordinary units the mass is given by—

$$M = \frac{e^2}{\pi c^2 R} \log \frac{SR}{R'}$$

where R is the radius of the ring, and R' is the radius of the cross-section of the ring. This makes the radius of cross-section extremely small in comparison with the radius of the ring.

The same assumptions lead to the conclusion that the gyroscopic properties of the ring electron are exactly those of a classical electron in an orbit having the same magnetic moment.

The Magnetic Moment of the Ring Electron.

For simplicity we may suppose that the electron is composed of a charge e distributed round a circle of radius a , and moving with angular velocity ω . Then the moment of the equivalent simple magnet is $\frac{1}{2}ea^2\omega$. If m denote the electro-magnetic mass of the electron its angular momentum will be proportional to $ma^2\omega$. Thus the magnetic moment will be proportional to the angular momentum multiplied by e/m . The quantum theory indicates $h/2\pi$ as the angular momentum, and assuming the factor proportionality to be $\frac{1}{2}$, the magnetic moment is found to be 92.7×10^{-22} E.M.U.

The magnetic moment of the magneton of Weiss is 18.54×10^{-22} , which is exactly one-fifth of the number given above. It is to be noted that the magneton of Weiss "is not in any way identified with the electron, but is an empirical quantity derived directly from the magnitudes of the susceptibilities of paramagnetic elements and compounds, and for such substances only; it has no meaning for diamagnetic substances." (Parson, p. 76). Thus the magneton is purely empirical, and not a mechanistic conception. In another place, however, the author has suggested that it may arise as a difference effect (H. S. Allen, *Phil. Mag.*, 1915, xxix., 718).

Parson has given an estimate of the radius of his magneton, starting from the assumption that the positive sphere of a large atom is nearly proportional to its "magneton number." He concludes that the radius of the magneton is about 1.5×10^{-9} cm. Assuming further that the velocity at the circumference of the magneton is equal to the velocity of light, the magneton moment $= \frac{1}{2}eac = 3.5 \times 10^{-19}$ E.M.U. This is far larger than the magnetic moment of the iron atom in the metal at saturation for which the value is 2×10^{-20} only; but on Parson's theory no atom, however many magnetons it contains, can have a moment greater than that of one magneton, and the moment of most atoms will be very much less than this, because the force between the magnetons in an atom will always tend to orient them, so as to make their resultant moment zero.

S. B. McLaren (*Phil. Mag.*, 1913, xxvi., 800; *Nature*, 1913, xcii., 165) found that a magneton of any cross-section or aperture has an angular momentum about its axis of $(8\pi^2/c) \cdot \frac{1}{2}N_e N_m$, where c is the velocity of light, N_e is the number of tubes of electric induction terminating on the surface, and N_m is the number of tubes of magnetic induction passing through the aperture. The applications which McLaren proposed to make "to the theory of complete radiation, spectral series, and the asymmetrical emission of electrons in the ultra-violet light" were apparently never published.

Conclusion.

If the arguments in favour of a ring electron prove convincing, an important conclusion follows as to the central portion of the atom. The facts of radio-activity indicate that β -particles have their origin in the nucleus of the atom. If, then, ring electrons are present near the centre of the atom it will be necessary to revise the prevailing view as to the small size and purely electrostatic field of the nucleus. I have suggested previously that the core of a terrestrial atom is large enough to exert appreciable magnetic forces. This is a natural assumption to make when the core contains both ring electrons and positive units, whatever may prove to be the nature of the latter. In this case it is no longer necessary to postulate the large positive sphere of the Kelvin-Thomson atom, which has been employed in Parson's theory. When the effect of the magnetic core is taken into account the difficulty found by Parson of reconciling Moseley's atomic numbers with the number of magnetons in the atom disappears.

"To the physicist a theory is a policy rather than a creed." The ring electron not only serves the purpose of explaining known results, but suggests further lines for investigation and experimental research.

In conclusion, I should like to emphasise the fact that when electrostatic forces alone are considered it is impossible to secure stationary electrons such as seem required in order to explain the facts of valency and stereochemistry, and the results of Compton and Rognley.

On the other hand, when magnetic forces alone are considered it is necessary to postulate molecular magnetic fields of extremely large intensity (10^7 gauss, Oxley and Weiss).

These difficulties may be overcome at one and the same time by assuming the action of both electrostatic and magnetic forces in connection with the core of the atom and the electron. We may then introduce stationary electrons exerting both electrostatic and magnetic attractions and repulsions. The energy of the molecular field would be partly electric, partly magnetic.

It remains to reduce the theory to a quantitative form by determining the magnetic moment of the ring electron and that of the core of the atom, and then separating the local molecular field due to the magnetic action from that due to electrostatic action.

VOLUMETRIC DETERMINATION OF REDUCING SUGARS.*

A SIMPLIFICATION OF SCALES' METHOD FOR TITRATING
THE REDUCED COPPER WITHOUT REMOVING IT FROM
THE RESIDUAL COPPER SOLUTION.

By W. BLAIR CLARK.

Biochemist, Cotton, Truck, and Forage Crop Disease Investigations,
U.S. Department of Agriculture.

(Concluded from p. 142).

D. Data.

In the following paragraphs and tables data are given regarding certain features of the method which the writer has had occasion to investigate during the course of routine work.

1. *Agreement of Reduplicate Titrations.*—Table I. gives the results of ten consecutive determinations on a certain invert sugar solution. The tests were carried out as already described, using 20 cc. copper citrate-carbonate solution, 10 cc. invert sugar solution, and heating for six minutes on an electric hot plate.

In Col. 2 is recorded the number of cc. of sodium thio-sulphate solution required by the excess of iodine solution. In the third column are the differences between these

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TABLE II.—Ratio of Reducing Sugar to Thiosulphate Solution Equivalent to the Copper Reduced.

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
Expt No.	Dex rose.	Iodine.	Na ₂ S ₂ O ₃	Na ₂ S ₂ O ₃ equivalent to reduced Cu. Cc.	Dextrose factor.		Dextrose deviation.		Means for columns.	
					Single tests.	Curve B.	Calculated from mean factor. Mgms.	From Curve B. Mgms.	8.	9.
1. (a)	1'00	10'00	11'90	0'61	1'64	—	-0'24	-0'18	—	—
(b)	—	—	11'78	0'73	1'37	1'35	-0'09	-0'01	—	—
(c)	—	—	11'76	0'75	1'33	—	-0'07	+0'31	-0'13	-0'060
2. (a)	2'50	10'00	10'70	1'81	1'38	—	-0'24	-0'12	—	—
(b)	—	—	10'60	1'91	1'31	1'32	-0'12	+0'01	—	—
(c)	—	—	10'70	1'81	1'38	—	-0'24	-0'12	-0'20	-0'077
3. (a)	5'00	10'00	8'60	3'91	1'28	1'28	-0'13	0'00	—	—
(b)	—	—	8'60	3'91	1'28	—	-0'13	0'00	-0'13	0'00
4. (a)	7'50	10'00	6'65	5'86	1'28	1'27	-0'20	-0'06	—	—
(b)	—	—	6'60	5'91	1'27	—	-0'14	+0'006	-0'17	-0'127
5. (a)	10'00	10'00	4'50	8'01	1'25	1'25	-0'02	+0'01	—	—
(b)	—	—	4'48	8'03	1'245	—	+0'005	+0'02	-0'01	+0'015
6. (a)	15'00	10'00	0'37	12'14	1'235	1'24	+0'13	+0'05	—	—
(b)	—	—	0'60	11'91	1'25	—	-0'16	-0'23	—	—
(c)	—	20'00	13'10	12'15	1'23	—	+0'14	+0'07	+0'04	-0'037
7. (a)	20'00	20'00	8'82	16'43	1'22	1'22	+0'47	+0'04	—	—
(b)	—	—	8'90	16'35	1'22	—	+0'35	-0'05	+0'41	-0'003
8. (a)	25'00	20'00	4'90	20'35	1'23	1'22	+0'36	-0'17	—	—
(b) (a)	—	—	4'52	20'73	1'21	—	+0'83	+0'29	—	—
(c)	—	—	5'00	20'25	1'235	—	+0'23	-0'29	+0'30	-0'057
9. (a)	0'00	10'00	12'50	0'00	—	—	—	—	—	—
(b)	—	—	12'52	0'00	—	—	—	—	—	—
(c)	—	20'00	25'20	—	—	—	—	—	—	—
(d)	—	—	25'30	—	—	—	—	—	—	—
Totals and mean	190'50	—	—	152'83	1'246	—	—	—	—	—

(a) Heat was low and time of heating was extended about one minute. This test was omitted in the totals and means of Cols. 2, 5, 6, a d 10.

TABLE I.—Variations in Reduplicate Titrations when Using the Modified Scales Method for Titrating Reduced Copper.

1.	2.	3.	4.	5.
Titration No.	Na ₂ S ₂ O ₃ required.	Na ₂ S ₂ O ₃ equiv. to reduced Cu.	Dif. Na ₂ S ₂ O ₃ Cc.	Dif invert sugar. Mg.
Blank	25'10	—	—	—
1.	3'83	21'27	-0'08	-0'096
2.	3'63	21'47	+0'12	+0'144
3.	3'70	21'40	+0'05	+0'060
4. (a)	3'90	21'20	-0'15	-0'180
5.	3'71	21'39	+0'04	+0'048
6.	3'80	21'30	-0'05	-0'060
7.	3'78	21'32	-0'03	-0'036
8.	3'80	21'30	-0'05	-0'060
9.	3'75	21'35	0'00	0'000
10.	3'61	21'49	+0'14	+0'168
		213'40		

(a) Owing to fluctuation of the voltage this test did not begin to boil for nearly 4'5 minutes, but the total period of heating was not lengthened.

figures and the blank test, these differences being the cc. of thiosulphate equivalent to the copper reduced by the invert sugar. Col. 4 shows the differences between the numbers in Col. 3 and the arithmetical mean of these numbers, taken to the nearest hundredth cc. In Col. 5 the figures of Col. 4 are converted into milligrams. of invert sugar by multiplying by the factor 1'2. Inspection of Col. 5 shows that the greatest deviation from the mean of the ten reduplications was less than 0'2 mg. of invert sugar, and that this largest deviation occurred in a test which did not closely follow the normal heating course. It will also be observed that seven of the ten tests differed

from the mean by less than 0'1 mg. of invert sugar. There seems to be no question but that the chief part of the observed variations is due to uncontrollable factors in the reduction process.

2. Ratio of Reducing Sugar to Thiosulphate Used.—It has been stated that the copper reduced in the copper citrate-carbonate solution, and consequently the thiosulphate equivalent to the copper, is very nearly proportional to the reducing sugar present. Variations from strict proportionality become significant only when the quantity of reducing sugar is quite small, less than 7 or 8 mg. in the reduction mixture. This is brought out in Table 11.

All the tests shown in Table II, except two of the blanks were made on the same day. Starting with (1) (a), those lettered (a) were run through in order as given, then those lettered (b), and finally those lettered (c). It was the intention to run three tests for each quantity of dextrose taken, but a quite unusual fluctuation of the heating current during a part of the afternoon rendered this impossible; so for the third set of tests those quantities of dextrose were used which had shown the greatest variations between tests (a) and (b).

In Col. 4 are entered the cc. of sodium thiosulphate solution used in titrating the excess of iodine. Col. 5 gives the differences between these figures and the means for the blank tests. (The blanks for 10 cc. and 20 cc. iodine were not combined). These figures in Col. 5 represent, therefore, the cc. of thiosulphate solution equivalent to the copper reduced by the dextrose, and consequently are a measure of the dextrose. Col. 6 gives the dextrose factors obtained by dividing the mg. of dextrose shown in Col. 2 by the cc. of thiosulphate in Col. 5. The mean of Col. 6 is obtained by dividing the total of Col. 5 into the total of Col. 2, test (8) (b) being omitted.

In Col. 8 are shown the deviations from the correct value of dextrose that would occur if the mean value of Col. 6 were used as the factor by which to multiply the

values in Col. 5. The minus sign indicates that the dextrose value so obtained would be too small by the given amount, while the plus sign indicates too large a value. Col. 10 gives the means of these deviations for each group of tests for a given quantity of dextrose.

3. *Effect of Time of Heating upon the Copper Reduction.*—In practical working the amount of heat applied to the reducing mixture may be varied by changing either the length of the heating period or the intensity and quantity of the heat. To determine the effect of moderate variations, tests were made as shown in Table III. From this table it can be seen that the time of heating is an important factor. It should be noted that the last two items are not comparable with the first three. Besides being carried out with a different volume of the reduction mixture, different solutions of invert sugar were used. As a result of these and other similar tests, of which those given are typical, it was decided to use in the routine work of this laboratory a reduction period of six minutes and a volume of 30 cc. made up of 20 cc. copper citrate-carbonate solution and 10 cc. test solution, the last suitably diluted when necessary. No quantitative determination was made of the effect of the volume of the reduction mixture.

TABLE III.—Effect upon Reduction of Copper by Invert Sugar when the Time of Heating is Varied. (a)

Time of heating Mins.	Vol. of red. mixt.	Thiosulphate solution used for:		
		10.0 mgrm. invert sugar.	20.0 mgrm. invert sugar.	25.0 mgrm. invert sugar.
		Cc.	Cc.	Cc.
4.5	25.0	14.32	8.20	—
5.0	25.0	14.12	7.79	—
5.5	25.0	13.98	7.44	—
6.0	30.0	—	—	9.00
7.0	30.0	—	—	8.93

(a) The several figures given for thiosulphate solution used are the means of three or more titrations. The reductions were made on an electric hot plate operating under quite constant voltage. The heating periods in these and all other tests mentioned in this article were measured with an interval timer graduated in one quarter minutes, and readily set to time operations with a variation of less than three seconds. Incidentally, it may be stated that this has been found to be an exceedingly convenient piece of apparatus to have in a laboratory, as it releases nervous energy for use in more profitable ways.

4. *Effect of Sucrose, Alcohol, and Formaldehyde upon the Copper Reduction.*—One of the claims made for the copper citrate-carbonate solution is that it is much less sensitive to sucrose, alcohol, and aldehydes than is Fehling's solution. Table IV. gives the result of some tests with sucrose.

TABLE IV.—Effect of Sucrose upon Copper Reduction, Using a Reduction Volume of 25.0 cc. and a Heating Period of 4.5 Minutes.

Period of 45 minutes.			
No. of test.	Sucrose taken, Mgrms.	Thiosulphate used, Cc.	
1.	0.0	20.60	
2.	50.0	20.60	
3.	100.0	20.60	
4.	250.0	20.27	

From these results it is seen that sucrose has no sensible effect unless present in great excess as compared with the reducing sugar to be determined.

In studying the effect of alcohol, there was used as a test solution 10.0 cc. of an alcoholic dilution made by adding to some 95 per cent alcohol its own volume of dis-

tilled water. The reduction mixture of 30.0 cc. was heated six minutes on the electric hot plate, two closely concordant tests requiring a mean of 26.33 cc. thiosulphate solution. The blank tests with water gave a mean value of 26.45 cc. thiosulphate. Thus the effect of the quantity of alcohol used is hardly appreciable and is in fact within the experimental error.

5.00 cc. portions of a 10 per cent formaldehyde solution which had been standing on the shelf for several months were used in reduction mixtures of 25 cc. volume, heated 4.5 minutes. The mean of two concordant tests was 22.6 cc. thiosulphate solution, while the corresponding blank tests with water gave a mean of 24.2 cc. The considerable quantity of formaldehyde present gave a copper reduction equivalent to that of about 1.87 mg. of invert sugar.

5. *Effect on Copper Reduction of the Czapek-Dox Nutritive Fluid.*—In the laboratory a considerable amount of routine work is being done in determining reducing sugars added to or developed in Czapek-Dox nutritive fluid and in a modified form of this fluid in which ammonium nitrate is substituted for sodium nitrate. For test purposes fluids of both forms were made up to double strength in all ingredients except carbohydrates, which were omitted entirely. Copper reduction tests were then made, using these fluids and comparing them with blanks in which distilled water was used. The results are shown in Table V.

TABLE V.—Effect on Copper Reduction of the Czapek-Dox and Modified Czapek-Dox Nutritive Fluids. Volume of Reduction Mixtures 30.0 cc. and Heating Period Six Minutes.

Test.	Thiosulphate solution required with 10.00 iodine.		
	Blank. Cc.	Unmodified solution, Cc.	Modified solution, Cc.
(a) ..	12.75	12.75	12.70
(b) ..	12.72	12.72	12.75
(c) ..	—	12.70	—
Mean ..	12.735	12.723	12.725

From these figures it is evident that the effect upon the copper citrate-carbonate solution of both the unmodified and the modified forms of this nutritive solution is in no wise different from that of distilled water.

Summary.

The foregoing article may be summarised as follows:—

1. There has been described a quick and simple iodometric method of titrating the copper reduced in copper citrate-carbonate solution in the original reduction flask.

2. Concentrations of solutions used and a definite method of procedure have been described for quantities of reducing sugars up to 75 mg. and principles pointed out for adapting the process to larger quantities of such sugars.

3. The accuracy is such that with care the results of duplicate determinations should not differ by more than 0.25 mg. reducing sugar. In routine work the writer finds the difference less than 1.0 mg. in the majority of cases.

4. The ratio of reducing sugar to copper is nearly constant, the greatest variation occurring in low values. Instead of using tables it is advised that each observer standardise his own procedure and then determine the ratio for that procedure.

5. Sucrose in quantities not exceeding 100 mg. per 10 cc., 50 per cent ethyl alcohol, and two modifications of Czapek's nutritive fluid have no appreciable reducing effect on the copper citrate-carbonate solution; but 10 per cent formaldehyde effected a small reduction of copper.

ORDER OF THE MINISTRY OF MUNITIONS.

SEEDS, OILS, AND FATS.

General Licence.

WITH reference to the Order made by the Minister of Munitions on May 1, 1917, relating to seeds, oils, and fats, which, amongst other things, prohibited, with certain exceptions, all purchases and sales of and dealings in the seeds, oils, and fats, specified in the first schedule to such Order, except under and in accordance with the terms of licences issued by or under the authority of the Minister of Munitions, the Minister of Munitions hereby gives notice that as from March 18, 1919, until further notice, he hereby licences all persons to sell, purchase, and deal in all or any to the seeds, oils, and fats specified in the first schedule of the said Order as they may think fit irrespective of quantity, subject only to the following condition, namely:—

No such sale, purchase, or dealing shall be effected at a price in excess of that fixed as the maximum price for such sale, purchase, or dealing by the said Order of May 1, 1917, as extended and modified by the subsequent Orders relating to seeds, oils, and fats made by the Minister of Munitions on May 9 and June 19, 1917.

This general licence may be cited as the "Seeds, Oils, and Fats General Licence, 1919."

NOTES.

(From the British Association of Trade and Technical Journals).

THE Alby United Carbide Factories, Ltd., Alby Electrode Works, Hebburn-on-Tyne, desire particulars of publications dealing with Amorphous Carbon Electrodes.

J. A. Hewetson and Co., Ltd., Timber and Hardwood Merchants, Dansom Lane, Hull, are contemplating manufacturing Plaster Picture Frame mouldings, which were previously imported from Germany. They have no knowledge of the procedure and want to get in touch with a publication dealing with this matter. Also information with regard to gilt slips and gilt flats, which are inserted in picture frames next to the moulding.

John Hart Brittain, Ltd., 2, Percy Street, London, W.1, desire the address of a manufacturer of tin filling machines suitable for use in filling tins with face cream, ointment, &c.

Hawkins Brothers, Melbourne Works, Coombe Street, Exeter, contemplate manufacturing wood bedsteads and bedding, and want particulars of makers of machines for carding wool, making wire mattresses, and ironwork complete.

Sir W. G. Armstrong, Whitworth, and Co., Ltd., Brass Foundry Dept., Elswick Works, Newcastle-on-Tyne, are desirous of obtaining an up-to-date book relating to Brass Sheet Rolling Mill Practice.

Safety Storage and Warehousing Co., Ltd., Douglas and Humboldt Streets, Victoria, B.C., want a copy of publications dealing with machinery for the following uses:—Extracting oil from Cotton Seed, Cocoa, and other beans, and Copra or coconuts; also wood pulp and paper making machinery. They also want the names of reliable firms who handle new and second-hand machines for these purposes. These machines are not made in Canada, but are obtainable from the U.S.A., but the enquirer prefers interesting his friends in British made machines rather than American.

Lieut. Norman Turner, 225th Mixed Brigade Train, Gorleston-on-Sea (Proprietor of H. Vickers and Co., Manufacturers of Ivory Billiard Balls and Accessories, 1, North Avondale Road, Southport), who up to the present time has been engaged in ivory turning, intends, on his release from the Army, laying down the necessary plant for Billiard Cue making, and wants any information regarding the manufacture.

E. B. Welster, 17, Gordon Square, London, W.C., is interested in Motor Tractors and desires particulars of publications dealing with the same.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 6, 1919.

Sir J. J. THOMSON, President, in the Chair.

The following papers were read:—

"Atmospheric Stirring Measured by Precipitation." By L. F. RICHARDSON.

"Measurement of Water in Clouds." By L. F. RICHARDSON.

Photometric methods enable us to estimate the amount of water in clouds in terms of the diameter of the cloud droplets. For thin cloud, through which the sun can be seen, it is the contrast of brightness between the sky and the sun which is measured. For thick uniform stratus it is the total light transmitted to earth which is measured as a fraction of the incident sunlight. If the cloud were compressed into a homogeneous horizontal lamina, of water or of ice according to its temperature, the thickness of this lamina would appear to have the following values, when expressed as a multiple of the diameter of the cloud droplets:—For cirrus, cirro-stratus, and cirro-cumulus on the average about 0.5; for stratus which only just permitted the sun to be seen, 4.1, the sun's zenith distance being 49° ; for a strato-nimbus of ordinary appearance, 24.

The formulae given are of the nature of first approximations. The apparatus is described. Incidentally, the scattering of sunlight by a sphere of water is studied in some detail.

Ordinary Meeting, March 13, 1919.

Sir J. J. THOMSON, O.M., President, in the Chair.

The following papers were read:—

"Concerning Emotive Phenomena. Part III.—The Influence of Drugs upon the Electrical Conductivity of the Palm of the Hand." By Dr. A. D. WALLER, F.R.S.

"The Existence of Daily Growth Rings in the Cell Wall of Cotton Hairs." By Dr. W. L. BALLS.

The probability that such growth-rings existed had been formerly deduced from studies upon the physiology and environment of the cotton plant in Egypt; but, since their thickness must be sub-microscopic, direct evidence was unobtainable until recently. By swelling the wall in hydration following formation of cellulose xanthate, by counting the layers thus magnified in thickness, and by comparative studies on the fuzz hairs, it is shown that each such ring corresponds to the cellulose laid down during one night's growth. The existence of variation as to kind or texture of cellulose thus shown to exist within the thickness of the wall, repeated some 25 times in the adult hair, necessitates reconsideration of many chemical and physical aspects of cellulose problems.

OBITUARY.

MONSIEUR JACQUES DANNE.

WITH great regret we have to announce the death of M. Jacques Danne, which took place at Gif (Seine-et-Oise), France, on March 8, at the early age of thirty-seven. M. Danne was Director of the Laboratoire d'Essais des Substances Radio-actives de Gif, and Editor of the well-known journal *Le Radium*. He was an enthusiastic worker in X-rays, radium, and the allied bodies, and has conducted many valuable researches on these subjects. His journal is one of the most important French periodicals devoted to this comparatively new science. He will be greatly missed by his fellow radiologists.

NOTICES OF BOOKS.

High Explosives. By Capt. E. DE W. S. COLVER, Dr. Met., F.C.S., A.I.A.E. London: Crosby Lockwood and Son. 1918. Pp. xx + 830. Price £3 3s. net.

THE copious literature in English, German, French, and Italian dealing with high explosives has certainly needed bringing together and summarising, and the author of this book has undertaken a formidable and lengthy task in attempting to deal with practically the whole of it. In the main he has succeeded admirably, although it would not be impossible to find details which could be adversely criticised. For example, the size of the book makes it rather unwieldy, and the same amount of material might well have been compressed into much less bulk, if all waste of space had been vigorously avoided, and possibly some unnecessary illustrations cut out. The treatment of coal-tar and petroleum for the recovery of various derivatives is first described in detail, and directions are given for the testing and analysing of raw materials used for making explosives. These directions are hardly full enough for the analyst to work from them, but on the other hand, they give a general outline of the processes usually adopted and the conclusions to be drawn from the results obtained. Methods of nitration are described, and separate chapters are given to the nitro derivatives of the aromatic hydrocarbons, the manufacture, purification, properties, &c., being fully discussed. The rules and regulations regarding the manufacture of nitro-compounds enforced in Germany are reproduced, and full accounts are given of the toxic effects of nitrous fumes, symptoms of poisoning, &c. The general properties of explosives their use and application, &c., are treated in considerable detail and from an eminently practical standpoint, and the book is bound to take rank as an exhaustive and authoritative text-book on the chemistry of high explosives and their uses for both military and industrial purposes.

BOOKS RECEIVED.

- "A System of Physical Chemistry." By Prof. W. C. MCC. LEWIS, M.A.(R.U.I.), D.Sc.(Liv.) Pp. vii + 204. Second Edition. In Three Volumes. Vol. III. "Quantum Theory." With two Appendices by JAMES RICE, M.A. London: Longmans, Green, and Co., 30, Paternoster Row. 7s. 6d. net.
- "Coal tar and some of Its Products." By ARTHUR H. WARNES. Pp. xxii + 102. London: Sir Isaac Pitman and Sons, Ltd.
- "An Advanced Course in Quantitative Analysis." With Explanatory Notes. By Prof. HENRY FAY. Pp. vi + 111. New York: John Wiley and Sons, Inc. London: Chapman and Hall, Ltd. 1917. 6s. net.
- "A Systematic Course of Qualitative Chemical Analysis of Inorganic and Organic Substances." With Explanatory Notes. By Prof. HENRY W. SCHIMPF. Third Edition, Revised. Pp. ix + 187. New York: John Wiley and Sons, Inc. London: Chapman and Hall, Ltd. 1917. 7s. net.
- "Essentials of Volumetric Analysis." An Introduction to the Subject. Adapted to the Needs of Pharmaceutical Chemistry. By Prof. HENRY W. SCHIMPF. Third Edition, Rewritten and Enlarged. New York: John Wiley and Sons, Inc. London: Chapman and Hall, Ltd. 1917. 7s. net.

Röntgen Society.—The Joint Meeting with the Faraday Society for the discussion on "The Application of X-rays to Engineering and Metallurgy," has been fixed for April 29, 1919. The time and place of the meeting will be announced in due course. It is hoped that members of the Röntgen Society will find it convenient to be present at the joint meeting.

CORRESPONDENCE.

NUCLEAR ATOMS.

To the Editor of the Chemical News.

SIR.—The structural alteration of the atom described by Prof. Soddy in the *CHEMICAL NEWS* of March 7, 1919, makes it possible for hydrogen to have a nuclear positive charge = 2 with one electron = 1, so that the net nuclear charge, representing unit atomic number, balances a single electron in the outer shell. Physicists, however, contemplate a single positive charge as the maximum nuclear charge of the hydrogen atom; but they are thereby faced with a dilemma. Either there are large numbers of charges at an identical point forming the nucleus of the heavier atoms, which many will agree is absurd; or the positive charges representing mass must be numerically doubled to enable the mass units to be stabilised symmetrically, as described in my "Chemistry an Exact Mechanical Philosophy," published in 1900. The fact that "Pope's (?) benzene nucleus" with its *ortho*-, *meta*-, and *para*-positions is anticipated in this work is evidence of a correct theory of the nature of chemical bonds.—I am, &c.,

FRED. G. EDWARDS.

MISCELLANEOUS.

Notice of Removal.—Messrs. Henry Faija and Co., of the Portland Cement Testing Works and Chemical Laboratories, request us to announce that they have left their premises in Old Queen Street, and now carry on business at 6, Earl Street, Westminster, S.W.

Royal Institution.—Next Thursday, April 3, at 3 o'clock, Prof. A. Findlay will deliver the first of a course of two lectures at the Royal Institution on "Colloidal Matter and its Properties." The Friday Evening Discourse on April 4 at 5.30 will be delivered by Prof. Frederic Harrison on "History of the City of Constantinople"; on April 11, Prof. Sir J. J. Thomson, Professor of Natural Philosophy, Royal Institution, on "Piezo Electricity and its Application."

Motor Transport Amenities.—Sir Eric Geddes, G.C.B., G.B.E., M.P., Minister-Designate of the new Ministry of Ways and Communications, Mr. Walter Long, M.P., in his capacity as Minister in Charge of H.M. Petroleum Executive, and Mr. W. Joynton-Hicks, M.P., will be amongst the principal guests at the Annual Luncheon of the Commercial Motor Users Association (Inc.) to be held at the Savoy Hotel on Wednesday, April 2.

MEETINGS FOR THE WEEK

- MONDAY, 31st.—Royal Society of Arts, 4.30. (Centor Lectures) "Problems of Food and their connection with Our Economic Policy," by Prof. H. E. Armstrong.
- TUESDAY, April 1st.—Royal Institution, 3. "British Entomology—The People of Scotland," by Prof. A. Keith.
Röntgen Society, 8.15. "Some Biological Effects produced by Small Quantities of Radium," by Dr. W. S. Lazarus-Barlow.
- WEDNESDAY, 2nd.—Royal Society of Arts, 4.30. "The Cultivation and Preparation of Flax, and the Linen Industry," by W. N. Boase, C.B.E.
Society of Public Analysts, 8.
- THURSDAY, 3rd.—Royal Institution, 3. "Colloidal Matter and its Properties," by Prof. A. Findlay.
Royal Society, 4.30.
Chemical Society, 8.
- FRIDAY, 4th.—Royal Institution, 5.30. "History of the City of Constantinople," by Frederic Harrison.
- SATURDAY, 5th.—Royal Institution, 3. "Spectrum Analysis and its Application to Atomic Structure," by Prof. Sir J. J. Thomson, O.M.

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THE CHEMICAL NEWS

VOL. CXVIII., No. 3077.

ESTIMATION OF CYANOGEN COMPOUNDS IN CONCENTRATED AMMONIA LIQUOR.*

By PERCY E. SPIELMANN, Ph.D., B.Sc., F.I.C., and HENRY WOOD.

THE methods of estimation of these substances in crude gas liquor have been either worked out or re-examined most carefully by Linder, whose valuable results have been published in various of the Alkali Inspector's Reports. They are, however, not immediately suitable for employment in the examination of concentrated ammonia liquor, partly on account of the large percentage of ammonia present, but particularly on account of the occasional smallness in quantity of one or other of the cyanogen impurities.

Determinations of considerable accuracy can be made very simply by a colorimetric method (compare Young, Alkali Inspector's 43rd Rep., 1906, p. 42), by employing the Lovibond tintometer.

The substances to be estimated are:—Ammonium thiocyanate: highest percentage met with 0.185 per cent, average quantity about 0.06 per cent. Ammonium cyanide ("volatile cyanide"): highest percentage met with 0.024 per cent. Ammonium ferrocyanide: highest percentage met with 0.44 per cent, average quantity about 0.1 per cent.

The usual titration method for estimating thiocyanate as coprous thiocyanate is scarcely admissible in the present connection, mainly on account of the end point being somewhat troublesome (*loc. cit.*, p. 47); thus the percentage of ammonium thiocyanate found in two successive examinations in concentrated ammonia liquor was 0.0538 per cent and 0.0526 per cent, and in crude liquor 0.237 per cent and 0.275 per cent.

Feld's method for estimating cyanide can be employed, but it is somewhat tedious; and it is necessary to modify it—on account of the large quantity of ammonia present—after adding to the liquid 50 cc. of concentrated lead nitrate solution, by neutralising the remaining ammonia by running in 2N nitric acid, until a little lead hydroxide still remains undissolved. Distillation and titration are then proceeded with as usual.

Feld's method of estimating ferrocyanides, though applicable, is lengthy and cumbersome as compared with Williams' elegant reaction with coprous chloride (*Journ.*, 1912, 468).

The basis of this scheme of analysis which is being advocated is the following:—

1. Conversion of the ammonium thiocyanate into ferric thiocyanate and measurement of the depth of colour obtained.

2. Interaction of a further quantity of the original liquid with ammonium polysulphide, whereby the ammonium cyanide originally present is converted into ammonium thiocyanate, and the estimation of the total ammonium thiocyanate as ferric thiocyanate. The increased quantity found over and above that found directly (without polysulphide treatment) is a measure of the quantity of cyanide originally present.

The presence of ferrocyanide compounds causes no complication, as the conversion of any proportion of the ferrocyanide into thiocyanate by the polysulphide solution can be avoided.

After a considerable number of experiments and trials on known mixtures and on commercial samples, the

following procedure is recommended, and it is advised that details be closely adhered to.

Estimation of Ammonium Thiocyanate.—10 cc. of the sample is run into about 40 cc. of water and the liquid is acidified with dilute sulphuric acid, shaking and cooling being continuous all the time. Iron alum is added until the liquid becomes red in colour, and it is then warmed to coagulate the precipitate. It is allowed to stand for half an hour, and after filtering and washing the precipitate, and cooling, 10 cc. of acid solution of iron alum (100 cc. of saturated alum solution with 10 cc. of concentrated nitric acid) is added, the volume is made up to 100 cc., and the liquid examined in the tintometer.

If the depth of colour is too great, the liquid must be diluted by taking 50 cc., adding 10 cc. more of the acid alum solution, and making up to 100 cc. If this further addition of iron alum be not made, the dilute solution is less than half as deep in colour as the stronger solution.

Estimation of Ammonium Thiocyanate together with Ammonium Cyanide, after Conversion of the latter into Thiocyanate.—If ferrocyanide is absent, 10 cc. of the sample is run into a little water, ammonium polysulphide solution is added until the liquid is distinct yellow, and the mixture is diluted to 100 cc. The polysulphide solution is made (Alkali Inspector's Rep., 1906, p. 47) by diluting 200 cc. of 0.880 ammonia to one litre, saturating half of this with hydrogen sulphide, adding the other half of the diluted ammonia solution, and then saturating with sulphur (which takes about a week). The liquid under examination is then heated to boiling-point, whereby all ammonia is driven off, treated with iron alum as before, and examined in the tintometer. The difference between this reading and that obtained for thiocyanate alone gives, by simple calculation, the percentage of cyanide in the original sample.

During the boiling stage, the precipitated sulphur occasionally becomes greenish. This does not indicate that there is necessarily any appreciable quantity of ferrocyanide in the precipitate; it may be due to a very small trace of sulphide of iron.

Estimation of Ammonia Cyanide when Ferrocyanide is present.—The removal of the ferrocyanide is carried out as follows: 25 cc. of the sample is run into polysulphide solution which is to be kept in excess as judged by its yellow colour. After standing for twenty minutes the liquid is acidified with dilute sulphuric acid, with continuous shaking and cooling (the latter precaution is important), and iron alum is added until the liquid becomes reddish in colour. It is then warmed (not above 60° C.) to coagulate the ferrocyanide precipitate; this is helped by the addition of a few crystals of sodium sulphate. After standing for half an hour, the precipitate is filtered off and washed as usual, and 50 cc. of acid iron alum is added to the filtrate. If the volume of the latter is about 500 cc. or more, a small addition of nitric acid is advisable.

The different procedures recommended for the estimation of thiocyanate and cyanide, when ferrocyanide is or is not absent, result from the necessity of avoidance of heating when ferrocyanide and polysulphide (added or original) are present together, or when cyanide may react, undesired, with polysulphide. It would be perfectly feasible, however, to employ the method given for the determination of cyanide when ferrocyanide is present to a sample when the latter is absent, but the procedure recommended is a quicker one.

Estimation of Ferrocyanide.—The precipitate obtained during the estimation in the previous paragraph consists of ferrocyanide and sulphur. This precipitate is treated according to the method given in the Alkali Inspector's 46th Report, 1909, except that after decomposition by sodium hydroxide, it is distilled according to Williams' method.

The applicability of the method, and its limitations, are shown by the following figures obtained from known mixtures:—In 5 cc. of a solution of potassium ferro-

* Reprinted from the *Journal of the Society of Chemical Industry*, February 28, 1919, xxxviii., p. 43.

cyanide containing 0.01840 gm. and 5 cc. of N/100 solution of ammonium thiocyanate the amount of ferrocyanide found was 0.01842 gm., whilst the same colour was obtained as when 5 cc. of thiocyanate solution was examined alone.

The behaviour of ferrocyanide towards polysulphide solution was tested by preparing a solution of ammonium ferrocyanide by precipitating a known quantity of potassium ferrocyanide with excess of iron alum, treating the washed precipitate with ammonia (sp. gr. 0.880), and converting into thiocyanate by boiling with polysulphide solution. The experiments showed that when ferrocyanide is present in only a very small quantity, the whole of it may be converted by the "hot method" into ammonium thiocyanate, making the cyanide figure too high; when, however, the ferrocyanide is present in a quantity above 0.001 per cent, an indefinite portion is converted, rendering results incapable of interpretation. The whole trouble may be avoided by using the "cold method."

Here the authors are in disagreement with Linder, who advocates (Alkali Inspector's 54th Rep., 1917, p. 25) boiling off the excess of volatile ammonium compounds from the mixture after reaction in the cold; their general experience of the reaction may be exemplified by the following figures obtained with a commercial sample:—Ferrocyanide, 0.0682 per cent; cyanide, absent; thiocyanate, running into boiling water (Linder's method), 0.180 per cent; boiling down, as usual, 0.180 per cent; by "cold method," 0.178 per cent; polysulphide, and boiling down (Linder's latest method), 0.300 per cent.

Without going further into the subject, it is of value to remember that the ferrocyanide precipitate appears to vary greatly in commercial samples of concentrated ammonia liquor, both in the ease or obstinacy of its appearance and formation, and in the velocity of its decomposition by sodium hydroxide.

Two artificial mixtures were made up and examined with the following results:—

No. 1.		
	Taken.	Found.
Ammonia 0.880	70 cc.	19.35 p.c.
H ₂ S passed in	—	1.25 p.c.
Ammonium thiocyanate solution	10 cc. = 0.076 p.c.	0.076 p.c.
Hydrocyanic acid (as KCN)	10 cc. = 0.0151 p.c.	0.0164 p.c.
Ammonium ferrocyanide solution	10 cc. = 0.0284 p.c.	0.0284 p.c.
Water	—	—
No. 2.		
	Taken.	Found.
Ammonia 0.880	50 cc.	14.25 p.c.
H ₂ S passed in	—	0.248 p.c.
Ammonium thiocyanate solution	10 cc. = 0.076 p.c.	0.074 p.c.
Hydrocyanic acid (as KCN)	1 cc. = 0.00151 p.c.	0.00141 p.c.
Ammonium ferrocyanide solution	5 cc. = 0.0076 p.c.	0.0076 p.c.
Water	34 cc.	—

The small discrepancies between the quantities taken and found are within the limits of accuracy of the method.

Estimation of Polysulphide.—Linder has described (Alkali Inspector's 54th Rep., 1917) how polysulphide in a sample of concentrated ammonia liquor can be estimated by its reaction with excess of cyanide to form an equivalent quantity of thiocyanate. This can obviously be determined by means of the tintometer, when the procedure would be the following:—(1) Determination of thiocyanate as such; (2) Addition of excess of cyanide solution and boiling as described above. In this case reaction of existing cyanide and ferrocyanide is of no consequence, as the final result is the conversion of polysulphide into thiocyanate. The difference between the

two results is the measure of polysulphide in terms of thiocyanate.

Mode of Employment of Tintometer.

In the usual practice of colorimetric methods it is customary to compare the colour obtained experimentally with that given by a known strength of the substance which is being estimated, and this usually entails making up at least one fresh standard for each experiment or batch of experiments.

When a tintometer is available and a considerable number of samples have to be examined, it is economical in time and trouble to measure once for all the depth of colours of known mixtures of various strengths and to record them on squared paper, so that any subsequent colour can be compared with the graph so constructed. In the present case the authors had a Lovibond tintometer in use, and this was found to be a very suitable instrument for the purpose.

The instrument was set up pointing to the interior of a box blackened on the inside, with a strip of truly white paper opposite the end of the instrument. Extraneous light was excluded from the front opening by a curtain of black velvet. Inside, a half-watt lamp was used as a source of illumination, screened with three thicknesses of truly white tissue paper in order to temper the light to a suitable intensity.

Measurements of depth of colour are made by matching the tint of the liquid with red and yellow glasses, but as a considerable latitude was found to be associated with the yellow colour, the strength of thiocyanate is best plotted against the red colour units only.

In making up the standard colours the following quantities of ammonium thiocyanate were taken, treated with acid iron alum and diluted to 100 cc. 1 cc. of N/10 ammonium thiocyanate contains 0.0076 per cent of the salt. Suitable quantities were diluted and measured in three cells, giving three different thicknesses of liquid.

Ammonium thiocyanate.		
Cells.	Per cent wt./vol.	Red units.
$\frac{1}{8}$ in. {	0.0019	1.3
	0.0076	4.6
	0.0300	13.65
$\frac{1}{4}$ in. {	0.0019	4.6
	0.0038	7.6
	0.0076	11.9
1 in. {	0.0019	7.6
	0.0038	13.0

It was found that above 12 or 13 units the colour was so deep that matching became uncertain. If colours requiring stronger glasses than those given are obtained they must either be measured in the cell of less thickness or further diluted (see *ante*).

It was found that under the conditions of testing the known solutions, the limit of sensitiveness of the eye was 0.15 red unit in the $\frac{1}{8}$ " and in the $\frac{1}{4}$ " cell, which is equivalent to 0.00221 per cent ammonium thiocyanate and 0.00007 per cent hydrocyanic acid. Therefore the figures found are as close as is possible.

The source of light was standardised on a solution of potassium bichromate, saturated at 20° C., in order that the present work and all other work with colours of the same order can be referred to a definite standard.

Source of illumination.	Cell.	Red units.	Yellow units.	Intrinsic brightness above standard (not affecting depth of colour).
$\frac{1}{2}$ -Watt-lamp (a)	$\frac{1}{8}$ in.	5.8	16.5	0.01
	$\frac{1}{4}$ in.	10.8	34.0	0.02
Daylight.. ..	$\frac{1}{8}$ in.	8.0	38.0	—
	$\frac{1}{4}$ in.	13.25	38.0	—

(a) Two different lamps were tested and found to be alike.

The following points in connection with the tintometer reading should be noticed:—Increased thickness of tissue paper for tempering the source of light increases the amount of standard yellow for matching the experimental liquid. A lamp with frosted glass is preferable to a plain glass bulb shielded with tissue paper. If the liquid is intrinsically brighter than the colour glasses neutral tint should be added, after which matching of colour is more reliable.

We take pleasure in acknowledging the courteous manner in which the experience of the Tintometer, Limited, has been placed at our disposal.

DISCUSSION.

Dr. H. G. COLMAN said that his experience with colorimetric methods for thiocyanate had not been satisfactory, testing with solutions containing known amounts of thiocyanate, but he had not tried the method using the tintometer, which might be more accurate. He asked the author whether with liquids such as these, containing phenols, the pink colour resulting from the action of the ferric salt on these did not interfere with the test, and whether phenols were added in testing the check solutions. He also asked if hydrogen sulphide was present in the check tests given for cyanide, as he and Yeoman had always obtained low results in its presence, although in its absence the results were satisfactory.

Dr. SPIELMANN, in reply, stated that it had been substantiated by direct experiment that the colour given by even 1 per cent of phenol and the subsequent addition of a little cresol had no appreciable detrimental effect on the method of analysis. In regard to the presence of hydrogen sulphide when making check tests it would be seen from the two examples given in the paper that this was present in both cases.

PHYSICAL CHEMISTRY AND ITS BEARING ON THE CHEMICAL AND ALLIED INDUSTRIES.*

By Prof. JAMES C. PHILIP, O.B.E., M.A., Ph.D., D.Sc.

THE field of physical chemistry, although now fully recognised as an integral part of chemical knowledge, has sometimes been regarded as lying entirely apart from that of industrial activity. This is a complete misconception, for while the influence of physical chemistry on the conduct of technical processes in the chemical and allied industries is, no doubt, indirect in the majority of cases, it is none the less real and extensive. Physical chemistry is concerned mainly with general underlying principles, but its development has contributed in a notable degree to the further advancement of chemical knowledge from the purely descriptive to the rational and quantitative stage. This is abundantly evident in the recent history of inorganic chemistry. Important reactions between well-known substances, reactions which twenty or thirty years ago were well understood in a general way, have been explored afresh in the light of physico-chemical principles, and an enormous amount of valuable quantitative data has been accumulated in this renaissance of inorganic chemistry.

In the chemical and allied industries, as elsewhere, one main element in progress and development is the gradual substitution of quantitative knowledge for qualitative, and the displacement of rule-of-thumb, haphazard methods by those which are based on scientific principles, and therefore permit intelligent control. In the advance so far made along these lines physical chemistry has played no small part, and it is the object of these lectures to emphasise

and illustrate some of the physico-chemical principles which have a definite bearing on industrial processes.

One of the main directions in which physical chemistry has led to a clearer perception of the optimum conditions and the working limits of technical operations is in connection with chemical equilibrium. Up till a comparatively recent time the best known chemical reactions were of the type which may be described as "complete" in the sense that the change proceeds until one at least of the necessary reacting compounds has been used up and has disappeared. This, perhaps, is not surprising, for the object of analytical chemistry—one of the prominent practical branches of the science—is to discover precisely those reactions which are complete, involving the quantitative conversion of some one substance into another. It is on the quantitative character of the change that the possibility of accurate analysis depends.

Physical chemists, however, have directed attention specially to those numerous reactions which may be described as "incomplete," in that the change stops short of the entire disappearance of any one of the reacting substances, and all the parties to the reaction are represented in the mixture finally obtained. A state of balance or equilibrium between the various substances concerned is established, and the reaction is accordingly termed an "equilibrium" or "balanced" reaction. In such cases it is further found that if the reaction products, or the "resultants," as they may be called, are brought together, they also interact to produce the original substances. The reaction, that is, may proceed in either direction, according to the relative proportions of the compounds concerned, and it may therefore be fairly described as a "reversible" reaction. It is customary to indicate the existence of this reversibility in any particular case by the use of a double arrow instead of the sign of equality, thus: $A + B \rightleftharpoons C + D$.

The further question now arises as to the factors which determine the position of the equilibrium in a reversible reaction, and to this question physical chemistry can supply a quantitative answer. Suppose, for instance, that the substances A, B, C, and D in the foregoing reaction are gases. Then, in accordance with the kinetic conception of the gaseous state, one must picture the molecules in a mixture of the four substances as in a constant state of motion, continually colliding with one another and impinging on the walls of the containing vessel.

Now chemical action between A and B will be possible only when a molecule of A collides with a molecule of B, and the progress of the change denoted by the upper arrow will depend on the number of these collisions occurring per unit of time—i.e., on their frequency. The frequency of collision, on the other hand, will be proportional to the numbers of the molecules of the substances A and B which are present in unit volume—i.e., to their concentrations. Hence, if the change is resolved into two component opposed reactions $A + B \rightarrow C + D$ and $C + D \rightarrow A + B$, and if v_1 denotes the velocity of the former reaction and v_2 that of the second, then $v_1 = k_1ab$, and $v_2 = k_2cd$, where a, b, c, d are the concentrations of the four molecular species A, B, C, and D at the moment considered, and k_1, k_2 are proportionality factors. These formulæ are the algebraic expression of the law of mass action.

For an observer it is not possible to isolate and follow the separate component velocities; he can determine only the net velocity of the total change—i.e., $v_1 - v_2$. As the reaction approaches its position of equilibrium, $v_1 - v_2$ becomes smaller and smaller, and, finally, when equilibrium is established, $v_1 - v_2 = 0$. This does not mean that the reaction mixture is in a condition of stagnation, that all collisions and interchanges have ceased; it means only that there is as much change in the one direction as in the other.

At equilibrium, then, $v_1 = v_2$ or $k_1ab = k_2cd$, a, b, c , and d being now the concentrations of A, B, C, and D in the equilibrium mixture. This equation may be written

* Canton Lecture (I.). Delivered before the Royal Society of Arts, December 2, 1918. From the *Proceedings of the Royal Society of Arts*, lxvii., No. 3450.

$k_1/k_2 = cd/ab$, or, since the ratio of two constants is itself a constant, $K = \frac{cd}{ab}$. This quantity K is termed the

"equilibrium constant" of the reaction, and its numerical value defines the position of equilibrium for $A + B \rightleftharpoons C + D$ at the temperature considered. This argument may be generalised, and the law of mass action leads to the conclusion that, however the individual concentration values may vary, $\frac{Y}{X} = \text{const. at any given temperature, where}$

X is the product of the equilibrium concentrations of the substances on the left-hand side of the equation, and Y is the product of the equilibrium concentrations of the substances on the right-hand side.

These considerations may be applied in the first case to the well-known and technically important equilibrium between sulphur dioxide, oxygen, and sulphur dioxide.

This may be represented as $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$, and is the reaction utilised in the large scale production of sulphuric acid by the so-called contact process. It has long been known that sulphur dioxide and oxygen, if passed together over heated platinum, combine to a large extent to form sulphur trioxide, and, indeed, an English patent for such a process was taken out in 1831. Many decades passed, however, before the process was satisfactorily established on the manufacturing scale, the delay being mainly due to difficulties experienced in purifying the sulphur dioxide and in keeping the platinum in full activity as an accelerator of the change.

In the last few years this contact process for the manufacture of sulphuric acid, previously exploited mainly in Germany, has undergone a rapid development in this country, and large quantities of "oleum," essential for the production of explosives, have been turned out. Sulphuric acid, however, is in large demand also in the times of peace, and it may be hoped that the various contact plants laid down under the pressure of war conditions will have a role to play when things are normal once again.

The possibilities and limitations of the contact process for sulphuric acid production cannot be thoroughly appreciated except on the basis of the principles of chemical equilibrium. These principles make it possible to formulate definitely the extent to which the equilibrium will be affected by varying the quantities of the reacting substances, and by altering the pressure and the temperature.

In the first place the law of mass action may be applied, on the lines already indicated, to the reversible reaction,

$2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$, or, as it may be written alternatively,

$2\text{SO}_3 \rightleftharpoons 2\text{SO}_2 + \text{O}_2$. If c_{SO_3} , c_{SO_2} , and c_{O_2} represent the concentrations of sulphur trioxide, sulphur dioxide, and

oxygen at the point of equilibrium, then $\frac{c_{\text{SO}_3}^2 \cdot c_{\text{O}_2}}{c_{\text{SO}_2}^2} = K$, the

value of which should be constant at a given temperature, irrespective of variations in the relative quantities of sulphur dioxide and oxygen initially used.

The validity of the foregoing mass action formula has been strikingly verified by an investigation in which mixtures of sulphur dioxide, oxygen, and nitrogen in varying proportions were passed through heated quartz vessels containing spongy platinum. The rate of flow was regulated so that the gases were long enough in contact with the hot platinum to attain the condition of equilibrium, and the values of c_{SO_3} , c_{SO_2} , c_{O_2} , the equilibrium concentrations, were deduced from a chemical analysis of the issuing gas mixture. Some results obtained at 727° may be quoted in order to show how closely the mass action formula represents the actual composition of the equilibrium mixture. In the following table, which embodies these results, the first three columns state the relative pro-

portions of the gases (sulphur dioxide, oxygen, and, in some cases, nitrogen) present in the initial mixture employed in each experiment: $2\text{SO}_3 \rightleftharpoons 2\text{SO}_2 + \text{O}_2$ at 727° .

Initial Gas Ratio.

SO_2	O_2	N_2	$K \times 10^3$
0.21	1	—	3.49
0.62	1	—	3.59
1.20	1	—	3.48
1.68	1	—	0.51
3.97	1	—	3.67
1.23	1	3.76	3.60
1.31	1	3.76	3.54
1.55	1	3.76	3.52
Mean			3.55

As shown clearly by these figures the value of K is independent (1) of the relative proportions of sulphur dioxide and oxygen in the initial gas mixture, and (2) of the presence or absence of nitrogen. In the course of the experiments it was further shown that the value of K obtained with a particular gas mixture was independent of the direction in which the equilibrium point was reached, and of the rate at which the gas was passed. It appears therefore that the mean value of K above may fairly be taken as a quantitative expression of the relation which at 727° exists between the equilibrium concentrations of the various substances concerned in the reaction.

When similar investigations are made at a series of different temperatures the values of K are found to exhibit a regular increase with rise of temperature, and thus form a record of the way in which the equilibrium shifts as the temperature conditions alter. The following table embodies the results of such experiments carried out at various points between 528° and 897°C. :—

$2\text{SO}_3 \rightleftharpoons 2\text{SO}_2 + \text{O}_2$ at Different Temperatures.

Temp. C.	$K \times 10^3$
528°	0.015
579°	0.077
627°	0.32
680°	1.12
727°	3.55
789°	12.6
832°	28.0
897°	81.6

If it is borne in mind that $K = \frac{c_{\text{SO}_2}^2 \cdot c_{\text{O}_2}}{c_{\text{SO}_3}^2}$, the increase

of K revealed by the foregoing figures plainly means that with rising temperature the equilibrium is shifted more and more in favour of the system $2\text{SO}_2 + \text{O}_2$; i.e., the dissociation of sulphur trioxide steadily increases.

From the values of K just tabulated it is easy to trace a graph representing the relation between K and the temperature, and from this to read off the value of the equilibrium constant at any desired point, such as 500° or 600° . The numerical value of K at this point being known it is then possible to calculate for any initial mixture of sulphur dioxide, oxygen, and nitrogen, what will be the composition of the equilibrium mixture; that is, to evaluate the mixture quantity—the "yield"—of sulphur trioxide obtainable under the given conditions. A series of such figures (see following table) shows clearly what are the optimum conditions—so far as the influence of temperature on yield is concerned—for the production of sulphuric acid by the contact process :—

Percentage Composition of the Initial Gaseous Mixture.

SO ₂ .	O ₂ .	N ₂ .
10.1	5.05	84.85
7.0	10.0	83.0
4.0	14.6	81.4
2.0	18.0	80.0

Percentage Conversion of Sulphur Dioxide to Trioxide at—

400°.	500°.	600°.	700°.
96.2	83.2	59.1	31.9
99.3	93.4	73.3	42.5
99.4	94.9	78.3	48.1
99.5	95.6	80.5	51.3

The figures just presented furnish the material for testing an interesting deduction that may be drawn from the equilibrium formula. If this is written in the form—

$$\frac{c^2}{SO_2} = \frac{1}{K} \cdot c_{O_2} \text{ or } \frac{c}{c} \cdot \frac{SO_3}{SO_2} = \frac{1}{\sqrt{K}} \cdot \sqrt{c_{O_2}}$$

it is plain that the proportion of trioxide to dioxide in the equilibrium mixture, at a given temperature, is proportional to the square root of the oxygen concentration, and will therefore rise as the latter is increased. This conclusion is confirmed by the figures in the table, for it is seen that, as the percentage of oxygen in the initial mixture increases relatively to that of the sulphur dioxide, the percentage conversion goes up.

(To be continued).

THE PERMANENT MARKING OF GLASS VESSELS.

By JOSEPH C. BOCK.

It is very often desirable and frequently necessary for the chemist to mark glass vessels permanently. This is usually done by means of a diamond or hydrofluoric acid. While the latter procedure gives good results if done carefully, it is a rather troublesome and lengthy process. The use of the diamond requires considerable practice in order to produce good markings, besides it is not always advisable to use it. A preparation called Diamond Ink, usually a mixture of ammonium fluoride, hydrofluoric acid, and barium sulphate, produces permanent marks and is easily applied. It is, however, difficult to obtain sharply defined markings with this method; furthermore the writing is not clearly visible if the surface becomes wet.

The present note proposes the use of glass colour fused in the glass by means of an ordinary burner. In glass painting, the glass colours, mostly mixtures of low fusing silicates and metallic oxides, are mixed with some vehicle and applied to the glass. They are then "fired" in a kiln at a temperature not exceeding 590° C. (Seger cone 022). This procedure is, of course, not applicable as such to ordinary laboratory conditions.

As the "firing" in the present method is done by means of a burner, many of the glass colours could not be used, because they undergo chemical changes when exposed to the flame.

In order to apply to the colours they are intimately mixed with a vehicle (made up of four parts copaiba balsam, one part clove oil, one part lavender oil). (The colours used are obtainable from the Roessler and Hasslacher Chem. Co., Ceramic Dept., Perth Amboy, N.J.—N. Y. Office, 100 Williams Street. The oil can undoubtedly also be obtained there. Many stores handling colours for china painting will have these materials on hand). The colours which have been found most suitable are—Green 728 D, Blue 1079 D, and a mixture of Brown

695 D, and White Enamel 1310 D. (Numbers refer to Roessler and Hasslacher products). The Brown alone can only be used on hard glass or porcelain where higher temperatures can be applied.

The actual procedure is herewith described—The glass colour (use Green 728 D) in powdered form is mixed with just enough of the oil, so it will still run from a pen. (Mixing can be done on a glass plate with a small spatula. Where a small amount of work is contemplated the indentations of an indicator tile have been found useful). A so-called crow-quill (steel) pen is recommended, a fine brush is also very good, but more difficult to handle. The desired markings are made on the clean glass surface. The marked article is then warmed evenly over a flame to dry the oil and also to prevent cracking in the final heating. The place where the marking has been made is now heated by holding against the side of the flame of a burner, the flame touching the marking on a tangent, the article being rotated part of a circle. (A Meker burner has been found best. The article should best be held near the base of the flame). During this heating the mark is watched carefully. The colour will first turn black through the carbonisation of the oils, then it will begin to glow a dull red. At this point the article is removed, allowed to cool a little and reheated until the markings, not the glass, again begin to glow.

The marking so obtained presents a smooth, shiny surface. It cannot be removed by mechanical or the usual chemical means. We consider the marking successful, when it cannot be removed mechanically (scratching or scouring), after a twenty-four-hour immersion in "cleaning mixture."

The paint should be mixed as thick as practicable. The heating must be done carefully to avoid caving in or other distortions of the vessel. If porcelain crucibles are to be marked the colour is applied as indicated above, the vessel is then heated in the usual way on a triangle over a free flame.

It may be of interest to mention some of the uses to which this procedure has been put. We have graduated test-tubes for special work, *p.e.*, for Benedict's colorimetric sugar method (12.5 cc. and 25 cc.) or graduated test-tubes to replace small graduated cylinders. Pipettes were graduated in the laboratory. Kjeldahl flasks may be marked to indicate the maximum volume to which they may be filled (students use). Beakers were graduated in 50 cc. or 100 cc. intervals. It is also advantageous to graduate distilling flasks roughly, to know the approximate liquid contents in the course of evaporation. The proposed procedure is especially valuable in the last mentioned instances, because any deep etching or engraving weakens the vessel.

The most difficult problem is the marking of microscope slides. Their heating requires great care and considerable experience in order to avoid an undue amount of breakage. They must be heated *over*, not on the side of a burner, the marked side towards the flame. It is our opinion that a muffle should be used where a large amount of slides are to be marked, using a strip of zinc (m. p. 412° C.) and a Seger cone 022, to indicate the temperature limits. Since a muffle furnace was not available we were unable to carry out this experiment. The marked slides, after being thoroughly dried, may be sent to some shop where glass firing is done and finished there for a nominal charge. (A semi-permanent marking medium can be obtained by mixing a pigment—lead oxide, lampblack, &c.—with a good spar varnish, canada balsam or collodion varnish—banana liquid. It will resist the ordinary cleaning and has been found useful for making stock bottles and similar containers).

[NOTE.—This method of marking vessels has been in use for many years at Sir William Crookes's laboratory for marking small porcelain crucibles and the quartz vessels used in fractional crystallisation of radio-active compounds. Enamel paints of various colours can be purchased at any good artist's colour shop, and it only needs

to be applied with a pen or a fine brush; the vessel is then heated to dull redness over a Bunsen or in a small muffle, and the mark becomes indelible.—*Journal of the American Chemical Society*, xli., No. 3.

THE USE OF ORTHO-TOLIDINE AS A COLORIMETRIC TEST FOR GOLD.*

By W. B. POLLARD,
Government Analytical Laboratory, Cairo.

ORTHO-TOLIDINE dissolved in dilute acetic acid was suggested by E. B. Phelps (Bulletin No. 1, Ohio State Board of Health, January, 1913) as a delicate colour test for free chlorine in water. This test was modified by J. W. Ellms and S. J. Hauser (*Analyst*, 1914, xxxix., 454), who showed that a hydrochloric acid solution of ortho-tolidine was better adapted for the purpose. Their reagent was prepared by dissolving 1 grm. of ortho-tolidine in a litre of 10 per cent hydrochloric acid.

This reagent in its modified form has now been found to be a delicate test for aurichloric acid. A solution of 1 part of gold in a million parts of water gave a bright yellow colour on addition 1 cc. of the reagent. With a solution containing 1 part of gold in 20 million parts of water the yellow colour can just be detected in a depth of 10 cms. of liquid.

Ellms and Hauser found that in the case of dilute solutions containing free chlorine the colour took about three minutes to fully develop, and was then permanent for about half an hour, after which it slowly faded. This was also found to be the case with aurichloric acid.

In making the test large amounts of strong mineral acid should not be present as the reaction becomes less delicate.

The following metals, when present as chlorides in a dilute hydrochloric acid solution, were found to give no reaction with ortho-tolidine:—Al, Sb(ic), Ba, Bi, Cd, Ca, Cr, Co, Cu, Ir, Pb, Mg, Hg, Mn(ous), Ni, Pt, K, Rh, Na, Sr, Sn(ic), U, and Zn.

In a second paper Ellms and Hauser point out that iron in the ferric condition also reacts with ortho-tolidine. The author found that in the case of ruthenium a yellow colour was also formed. Osmic acid gives a yellow colour, but this changes to green on standing. Vanadates acidified with dilute hydrochloric acid give a reaction. Molybdates acidified with hydrochloric acid do not react.

Sodium tungstate acidified with dilute hydrochloric acid gives a precipitate on addition of ortho-tolidine, but no yellow colour develops.

In preparing standard chlorine solutions Ellms and Hauser found that it was necessary to employ specially purified distilled water. This was not found to be so necessary in the case of gold solutions. The more dilute gold solutions should, however, only be prepared when required, and should contain a small amount of free hydrochloric acid.

In testing solutions which have been obtained by the use of *aqua regia*, special care should be taken to guard against the possible presence of free chlorine or of nitrous acid. The latter not only reduces gold solutions but gives a yellow colour with ortho-tolidine. Any reagents used should always be tested for reducing impurities; thus, on one occasion a sample of "pure" ammonium chloride completely reduced a weak gold solution.

In presence of much copper a green colour is obtained instead of a pure yellow; colorimetric comparison can, however, still be made if the standard gold solution is tinted with copper to a similar extent.—*Analyst*, xlv., No. 516.

THE PRODUCTION OF NITROGEN COMPOUNDS.*

By JACK P. MONTGOMERY, Department Chemistry
and Chemical Engineering, University of Alabama.

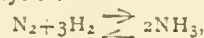
IT is the purpose of this paper to review the sources of nitrogen compounds, and the processes of utilising them, which are being employed to successfully meet, and in many directions more than meet, the unavoidable waste of nitrogenous material.

The most important of the compounds of nitrogen by the production of which the nitrogen equilibrium may be restored are nitrogenous organic compounds produced in agriculture, ammonia and ammonium salts, nitric acid, nitrates, and oxides of nitrogen. The sources from which these compounds may be derived are the sodium nitrate deposits of Chile, bituminous coal, various by-products of food production such as cotton-seed meal and the "tankage" from packing houses, and, of late, atmospheric nitrogen.

The production of nitrogenous organic compounds in agriculture depends upon the use of a fertilising material containing available nitrogen, or compounds which may become available in the soil, or upon the direct utilisation of the nitrogen of the atmosphere in the growth of the plant. The use of seed meals and of tankage as fertilisers is becoming less each year as these materials are being used more and more as feed stuffs. This makes it increasingly necessary that such nitrogenous materials as ammonium salts and nitrates be used, or that atmospheric nitrogen be made available. The direct utilisation of atmospheric nitrogen by plants or other living organisms appears to be possible only in the symbiosis of certain bacteria upon the roots of leguminous plants. The bacteria are able to convert the atmospheric nitrogen into compounds available for themselves and to store up in nodules upon the roots of the peas, beans, clover, or vetch reserve supplies of nitrogenous materials more than ample for the growing needs of the plant. These nodules remaining in the soil undergo the same kind of change as would other organic nitrogenous matter, and are transformed into ammonium salts or nitrates which may be utilised by following crops. This is the oldest and by far the most important of the methods for the fixation of atmospheric nitrogen. Obviously no figures are obtainable, but it is easily conceivable that under proper agricultural control this one method is capable of making good all the nitrogen waste which is normal to times of peace. The chief objection to this natural method for the fixation of nitrogen is that it requires time. The artificial methods for the fixation of atmospheric nitrogen into ammonia and nitric acid or ammonium salts and nitrates appeal more to the imagination and have of late received more attention, but we will do well not to forget this very important agricultural method.

There are two well-defined processes for making ammonia from atmospheric nitrogen, the synthetic or direct process, and the cyanamide or indirect process. Many attempts had been made to directly combine nitrogen and hydrogen, by sparking a mixture of the two gases, by heating with a catalyst, and so on, before the present synthetic process was developed by Haber and his associates. The success of the Haber process is due to great technical development accompanied by close attention to theoretical considerations.

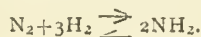
Nernst made an exhaustive study of the equilibrium conditions in the system—



and found that a higher pressure results in a greater ammonia concentration, and that certain catalytic agents favoured the forward action. Haber, by a careful development of the work of Nernst, found the most favour-

* Read at the meeting of the Society of Public Analysts, February 5, 1919.

able temperature and pressure conditions, and used, at first, osmium as a catalyst. This process was developed in Germany by the Badische Anilin und Soda Fabrik, a corporation which was highly subsidised by the Government. As far as has been revealed this process is known to take place in a cylindrical reaction chamber surrounded by an electrical heating resistance. The catalyst used now is probably a cheaper one than osmium. This is put into the reaction chamber, which is maintained at a temperature of 500° C. Nitrogen, obtained by the fractional distillation of liquid air, and hydrogen, made by the action of steam on iron at 300° C., are mixed in the proportion of one volume of the former to three of the latter, compressed to 200 or 225 atmospheres, and passed through the reaction cylinder. About 8 per cent of the materials present are converted into ammonia. This must be constantly removed or the reaction will come to a halt by the establishment of equilibrium in the system—



The ammonia is removed by passing the mixed gases through a condenser where the ammonia is liquefied and removed, the remaining nitrogen and hydrogen being continually worked over with fresh supplies added from time to time.

The development of this process is believed to have a very great bearing upon Germany's ability to supply herself with munitions of war. Ammonia made by this process is converted into nitric oxide and nitrogen peroxide, by a process to be described presently, and these in turn are made into nitric acid and nitrates.

A synthetic process developed by the General Chemical Company, a process believed to be a modification of the Haber process, will be used at the Nitrate Plant No. 1 at Muscle Shoals. In this plant a part of the ammonia will be oxidised to nitric acid, and the remainder will be combined with the acid in the formation of ammonium nitrate. While this is as yet an experimental plant, it is expected that the production will be large and that other plants of the same kind will be established at other points. Although this is a "war plant," it is expected that the product will be available for use as fertilising material. This process is expected to furnish ammonium nitrate at a lower cost than is possible with any other process, and we are awaiting the outcome of the experiment with great interest.

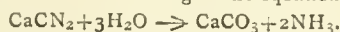
Indirect Method First Tried.

While the Haber process is of great theoretical and practical interest it must be remembered that the indirect or cyanamide process was the pioneer method for making ammonia from atmospheric nitrogen. Frank and Caro sought to make cyanide for gold extraction, obtaining the nitrogen from the air. Although not directly succeeding in this, they worked out a process the main feature of which was a method of fixing atmospheric nitrogen in a compound, calcium cyanamide, which in turn can be used in the manufacture of ammonia. In the cyanamide method calcium carbide, with the manufacture of which you are familiar, is treated in an electric oven with atmospheric nitrogen. About three-quarters of a ton of carbide is treated per oven, and the reaction is started by using the oven as a sort of resistance furnace, the charge of carbide being employed as the core offering resistance to the current. After a temperature of about 1000° C. is reached the reaction, being exothermic, proceeds to completion according to the equation—



After cooling, the cyanamide charge is crushed and any residual carbide is removed by careful hydration. The ammonia is then produced by treatment with steam in an autoclave. About four tons of cyanamide are charged into the autoclave containing a dilute caustic soda solution. Steam is admitted to the autoclave, and a pressure of 200

to 250 pounds maintained for some hours. The steam and cyanamide react according to the equation—



When the autoclave valves are opened the escaping gas is about one-fourth ammonia and three-fourths steam. The mixed gases are passed into condensers and the water and ammonia separated. The nitrogen for this process, as for the synthetic process, is made by the fractional distillation of liquid air.

The Nitrate Plant No. 2 at Muscle Shoals, just been completed by the Air Nitrates Corporation, will employ this process. This plant consists of a series of factories for the manufacture of lime, carbide, liquid air, cyanamide, ammonia, and nitric acid, the latter being made by the oxidation of the ammonia. The building of this immense fixation plant has challenged the attention of the whole country because of the rapidity of the construction of such an excellent and complete series of factories, any one of which would reflect great credit upon those undertaking such a task. While this plant is a monument to American efficiency in engineering, it remains to be seen whether or not, with the country on a peace basis, it will be required or whether it can be made to pay. It should be said, however, that this is by no means an experimental plant. Every process has been well tried out, and its success or failure will depend entirely upon economic conditions of cost of materials and labour and selling price of the product. This plant will have a rated capacity of 2,000,000 pounds of nitric acid per day. The only question is, can we in piping times of peace use all of it?

Ammonia produced by these methods is usually spoken of as being an artificial nitrogen product as distinguished from the ammonia from the "natural" source, coal. Until a year or two ago, when the artificial methods of producing ammonia overtook it, the production of ammonia and ammonium salts in connection with the by-product distillation of coal was the most important source of nitrogen with the exception of the sodium nitrate from Chile, which was, and still is, the most important source. During the period from 1914 to November, 1918, so far as obtainable figures show, the production of by-product and gasworks ammonia increased only 16 per cent. Of this increase Germany is to be credited with the greatest contribution. The relatively small increase in America and the lack of any increase at all in Great Britain was no doubt due to the fact that a by-product coal distilling plant requires such a considerable expenditure of capital and such an outlay of structural material that developments along this line were not to be undertaken during the war. But the potentialities of ammonia from this natural source are very great. At present comparatively little of our American coke is being produced in by-product ovens. As more and more of the beehive ovens are replaced by the by-product plants this source of ammonia will attain greater relative prominence because of its cheapness. By-product distillation of coal is, as an industry in this country, still in its infancy, and even though we marvel at the present feats of our engineers in that line, another decade will see these very wonders eclipsed. With the great development along this line which is bound to come, stimulated, we trust, by the lusty growth of the American dye industry, we may expect to see coal rank as a highly important source of nitrogen and outstrip in pounds produced not only ammonia by fixation but the nitric acid from sodium nitrate.

Even now it appears to some of us that if the same amount of constructive energy had been directed to the development of by-product coke plants in this country as has been devoted to the development of fixations plants we would be farther along the road of preparedness. We could have gone just as far in solving our nitrogen problems and would at the same time have saved much valuable material that has gone to waste in the beehive ovens. We might have learned a great deal by paying attention to the by-product situation in Germany. In

1910 Germany was producing 400,000 tons of ammonium sulphate, a little more than one-third of the entire world production. While accurate figures since the war began are not to be had, it is known that the by-product coke industry in Germany has greatly expanded, and there is reason to believe that they had reached an annual production of 1,000,000 tons of ammonium sulphate, or about one-half of the world's production, by the middle of the present year. Much of this material was used in the manufacture of munitions, and Germany did not have to depend too largely upon artificial nitrogen compounds.

(To be continued).

SEED MIXTURES FOR LAND AFFECTED BY CLOVER SICKNESS.*

OWING to the high cost of nitrogenous fertilisers, farmers should endeavour to conserve nitrogen by every means possible. Leguminous plants should therefore take a prominent place in every rotation. It is well known that in many districts red clover is liable to become "clover sick" if sown on the same field at too short intervals. It is probable that none of the leguminous forage plants are absolutely safe from attacks of "clover sickness," but it is evident that red clover is the most susceptible. Peas or beans, both valuable crops under existing conditions, could with advantage be introduced into the rotation on land that is known to be "sick" provided that it is at the same time suitable for the production of these crops, while in the formation of rotation leys, plants other than red clover should be used on "sick" land; or a mixture consisting only partially of red clover should replace large seedings of red clover by itself. Alsike clover, white clover, and trefoil do not suffer from "clover sickness" to nearly the same extent as red clover, and may therefore be used as substitutes for red clover.

Moreover, there is reason to believe that English grown late flowering red clover in particular and also broad red clover, from seed harvested in England, are less susceptible to "clover sickness" than imported clover. When, therefore, red clover is used at all in mixtures for "sick" land it is desirable that every endeavour should be made to secure home-grown stocks of seed for the purpose. On (chalky) soils, or in regions of comparatively low rainfall, trefoil may be largely used, while in districts of high rainfall more reliance should be placed on Alsike clover. The following mixtures are suggested:—

One Year Leys.—

	Lbs. per acre.		Lbs. per acre.
Chalky soils or low rainfall—			
Red clover ..	4	} or {	Alsike clover .. 4
Alsike clover ..	6		Trefoil 12
Trefoil	6		
High rainfall—			
Red clover ..	4		
Alsike clover ..	8		

It appears also from experiments conducted in Yorkshire and from experience elsewhere that red clover grown in conjunction with rye-grass is less susceptible to sickness than when grown pure; in districts adapted for growing mixed "seeds" the clovers might be decreased to half the above quantities and half a bushel of Italian rye-grass added to the mixture.

Two Year Leys.—White clover should be more largely relied upon in mixtures for two year leys, in which mixtures both Italian and perennial rye-grasses would also take a prominent place.

	Low rainfall, lbs. per acre.	High rainfall, lbs. per acre.
Red clover ..	2	2
Alsike clover ..	3	4
White clover ..	2	2
Trefoil ..	3	—
Italian rye-grass ..	6	6
Perennial rye-grass ..	4	4

On soils where giant sainfoin (see *Leaflet No. 280*) is known to succeed, especially where it has not been grown for a number of years, this crop sown pure might usefully replace red clover on "sick" land, whilst the value of lucerne (see *Leaflet No. 160*) on soils that suit it must, in this connection, be strongly emphasised. The vetch (see *Food Production Leaflet No. 51*) is another valuable leguminous plant which, as well as providing nitrogenous residues for the benefit of subsequent crops in the rotation, has a special value at present from the point of view of adding to the diminished supplies of hay. (*Leaflet No. 184* on red, white, and Alsike clovers may also be consulted).

London, S.W. 1, February, 1919.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 20, 1919.

Sir J. J. THOMSON, O.M., President, in the Chair.

The following papers were read:—

"Magnetic Storms of March 7-8 and August 15-16, 1918, and their Discussion." CHARLES CHREE, Sc.D., F.R.S.

The paper contains a discussion of two magnetic storms—the first on March 7-8, the second on August 15-16, 1918. For the March storm curves were utilised from Kew, Eskdalemuir, and Agincourt (Toronto) Observatories. For the August storm Kew and Eskdalemuir curves were alone available. The storms were of the same general type as one which occurred on December 16-17, 1917, and was discussed in a previous paper; but, unlike the previous storm, they both had conspicuous Sc's. ("sudden commencements"). The movements constituting the Sc. on August 15-16 were unusually large and their oscillatory character was very prominent at Agincourt and Eskdalemuir. In both cases, as in the storm of December, 1917, disturbance was much larger at Eskdalemuir than at Kew, especially in the vertical force. The declination changes at the two places showed rather a close resemblance, but the variations in the other elements differed at times not merely in amplitude, but in general character. The disturbance at Agincourt on March 7-8 was similar in intensity to that at Eskdalemuir, but conspicuously different in many details. There were some exceedingly large and rapid changes, especially of declination and horizontal force, at Agincourt, the range of the former element being about $2^{\circ} 5'$, as compared with $51'$ at Kew. Some consideration is given to the resemblances and differences between these storms and some mean results for storms having Sc's. given in a recent paper by Dr. S. Chapman.

"The Transparency of Biotite to Infra-red Radiations." By L. C. MARTIN.

The paper describes a curious reversible variation with temperature in the infra-red transmission of biotite. The infra-red apparatus employed was designed by Prof. Callendar and Mr. A. Eagle. Its optical properties are examined. Tables and curves showing the variation in transmission of biotite with wave-length at various temperatures are given and certain possible explanations are examined. The general nature of the effect is a halving of the transmission for a rise in temperature of about 200°C .

* Board of Agriculture and Fisheries, Food Production Leaflet No. 51.

PHYSICAL SOCIETY.

Annual General Meeting, February 14, 1919.

Mr. W. R. COOPER, M.A., B.Sc., in the Chair.

IN opening the meeting the Chairman referred to the loss the Society had sustained by the death of Prof. G. Carey Foster, one of the founders, and mentioned that the President, Prof. C. H. Lees, was representing the Society at his funeral that afternoon.

The Report of the Council was read by Prof. W. Eccles.

The Report of the Treasurer was read by Mr. W. R. Cooper.

Both reports were unanimously adopted.

While the ballot papers for the election of Officers and Council were being collected and counted, votes of thanks were accorded to the Honorary Auditors, the Officers and Council, and the Governors of the Imperial College, the respective proposers and seconders being Mr. C. C. Paterson and Dr. Bryan, Prof. Fortescue and Dr. Makower, Prof. Howe and Dr. Owen.

Mr. E. H. Rayner moved and Mr. W. R. Cooper seconded a vote of thanks to Prof. W. Eccles for his past services as joint honorary secretary.

The scrutators announced the result of the election of Officers and Council for the ensuing year:—

President—Prof. C. H. Lees, D.Sc., F.R.S.

Vice-Presidents (who have filled the office of President)

—Prof. R. B. Clifton, M.A., F.R.S.; Prof. A. W. Reinold, C.B., M.A., F.R.S.; Sir W. de W. Abney, R.E., K.C.B., D.C.L., F.R.S.; Prin. Sir Oliver J. Lodge, D.Sc., F.R.S.; Sir Richard Glazebrook, C.B., D.Sc., F.R.S.; Prof. J. Perry, D.Sc., F.R.S.; C. Chree, Sc.D., LL.D., F.R.S.; Prof. H. L. Callendar, M.A., LL.D., F.R.S.; Prof. A. Schuster, Ph.D., Sc.D., F.R.S.; Sir J. J. Thomson, O.M., D.Sc., F.R.S.; Prof. C. Vernon Boys, F.R.S.

Vice-Presidents—Prof. W. Eccles, D.Sc.; Prof. J. W. Nicholson, M.A., D.Sc., F.R.S.; Prof. O. W. Richardson, M.A., D.Sc., F.R.S.; R. S. Willows, M.A., D.Sc.

Secretaries—(*Papers*) H. S. Allen, M.A., D.Sc., 5, Presburg Road, New Malden; (*Business*) F. E. Smith, O.B.E., F.R.S., National Physical Laboratory, Teddington.

Foreign Secretary—Sir Richard Glazebrook, C.B., D.Sc., F.R.S.

Treasurer—W. R. Cooper, M.A., B.Sc., 82, Victoria Street, S.W. 1.

Librarian—S. W. J. Smith, M.A., D.Sc., F.R.S., Imperial College of Science and Technology.

Other Members of Council Prof. E. H. Barton, D.Sc., F.R.S.; Prof. W. H. Bragg, C.B.E., M.A., F.R.S.; C. R. Darling, F.I.C.; Prof. A. S. Eddington, M.A., M.Sc., F.R.S.; D. Owen, D.Sc.; Major C. E. S. Phillips, F.R.S.E.; E. H. Rayner, M.A.; S. Russ, D.Sc.; T. Smith, B.A.; F. J. W. Whipple, M.A.

After the conclusion of the general business, Prof. LEES took the Chair.

A paper entitled "*Temperature Coefficient of Tensile Strength of Water*," by S. SKINNER M.A., and R. W. BURFITT, B.Sc., was read by the latter.

The liquid is forced under pressure through a capillary constriction between two limbs of a U-tube. By trial the pressure is adjusted until the speed in the capillary is sufficient to produce rupture. This is judged by the sound and also the appearance. The whole U-tube is immersed in a bath, the temperature of which can be varied. Actual observations of rupture, velocity, and temperature are recorded up to about 100° C., from which it is deduced that the tensile strength becomes zero in the neighbourhood of 245° C., which is in agreement with theory.

DISCUSSION.

Dr. VINCENT asked what arrangements were made to get the liquid back into the virgin state after it had been churned up by forcing through the capillary.

Dr. BRYAN asked how dissolved gas affected the results. In experiments by Worthington and others the water required to be very carefully boiled before it showed any tensile strength at all.

Prof. LEES also commented on the fact that the liquid experimented on here contained dissolved gas. In Worthington's experiments with gas-free water the tensile stress was about 2 atmospheres, as far as he remembered. This seemed of a different order from that obtained by the authors.

Mr. F. J. W. WHIPPLE asked where the tensile strength came into the formula. The diagram seemed to connect velocity and temperature only.

Mr. BURFITT, in reply to Dr. Vincent, said the liquid was always allowed to stand until all cloudiness had disappeared, and any dissolved gas was in equilibrium. There was no doubt the presence of dissolved gas promoted rupture. Worthington's measure was static, and there was no danger of air getting in if the liquid was initially air free. In the present method it was impossible to prevent some air becoming dissolved. With reference to Mr. Whipple's comments, the tables are not primarily intended to give actual values of the tensile stress, but to give its variation with temperature. If desired, the value of C in the theoretical formula can be calculated from the figures given.

A paper entitled "*Vector Diagrams of Some Oscillatory Circuits Used with Thermionic Tubes*," was read by Prof. W. H. ECCLES.

The method of the crank or vector diagrams used commonly in the study of alternating-current circuits is applied in the paper to the assemblage made up of an oscillator, the thermionic relay maintaining it in oscillation, and the devices linking these two parts. The diagrams then serve as substitutes for the usual treatment of the problem by differential equation, and from them may be obtained all the formulæ. They have, besides, the advantage of exhibiting to the eye the phases of the currents and voltages in every part of the circuits. In forming the diagrams the potential drop across the oscillator is calculated by the usual rules of the alternating-current diagram, and added geometrically to the potential drop across the tube. This total is made equal, in magnitude and phase, to the voltage applied at the instant to the grid multiplied by the voltage factor of the relay. In its turn the voltage applied to the relay depends upon and is obtained from the current running in a portion of the oscillator. The fitting together of these lines gives all the conditions to be satisfied for the maintenance of steady oscillations.

DISCUSSION.

Prof. G. W. O. HOWE agreed that you could not really understand the conditions in a circuit unless you were able to put down the currents and voltages in a vector diagram. He had attempted himself to simplify Vallauri's treatment for students, but without as much success as Dr. Eccles. He had usually looked at these circuits from this point of view: The oscillatory circuit apart from the valve has a certain equivalent resistance. To maintain oscillations the equivalent of a negative resistance must be introduced. There are two ways of varying the current in the bulbs; the P.D. on the terminals or on the grid may be varied. In the latter case the current may be increased even if the total P.D. on the bulb is diminished, and if this condition can be arrived at we have the equivalent of a negative resistance to the oscillations. You have to arrange a coupling device so that the variations of current in the plate circuit produces suitable variations of potential of the grid. From the characteristic of the plate circuit you can determine the critical value of the mutual inductance between plate and grid circuits to give the equivalent negative resistance necessary for maintenance of steady oscillations.

Prof. C. R. FORTESCUE said the method of approach appears to be a distinct advance, in that the idea of the

tube as a generator of an E.M.F., gEg , enables a voltage diagram to be plotted instead of the more usual current diagram. This is an undoubted advance, and simplifies the final adjustment of the diagram to suit the conditions of the tube and circuit. At various times many vector diagrams have been drawn for various oscillatory circuits; and in the whole the results have hardly come up to expectations. There appears to be three reasons for this, viz.: (a) In order to draw the diagram at all a very clear insight into the conditions is required. In other words, it is necessary to know the final result before the diagram is completed. In the diagram of Fig. 3 of the paper it is necessary to know, firstly, that the angle θ is a positive angle, and, secondly, that the effective E.M.F. of the tube is in phase with the voltage applied to the grid. The latter condition is, of course, obvious from the action of the tube, but the former is by no means obvious, and has to be discovered by trial and error. If, for example, the current I is considered to be flowing through the inductance, then θ must be taken as an angle of lag, as will be found if an attempt is made to plot out this diagram. (b) The quantities are such that it is impracticable to plot the diagrams to scale. For example, if the numerical values of the first example on page 3 are taken, the ratio of the length of the line OUg of Fig. 3, to the length DQ is of the order of 1 to 500,000. Actually, if Fig. 3 is plotted to scale, it becomes a diagram vertically up and down the board. (c) Finally, there is the common experience of the sign difficulty in drawing the diagrams. There are many possibilities of confusion with the ordinary current diagram, but it is possible that with the author's voltage diagram these troubles will be very much reduced. It would appear that the true function of these diagrams, when numerical values are applied or when the diagrams are drawn to scale, is to justify the practical method commonly used of regarding the valve as a power supply. The anode current is in phase with the voltage across the oscillatory circuit. Taking the alternating components only, the product of the anode current and the circuit voltage gives the power supplied to the circuit. The anode current depends upon the anode and grid voltages, i.e.,

$$i = h_a e_a + h_{ge} e_g$$

as given on page 1 of the proof of this paper. To within a small percentage this power is absorbed by the circuit losses. If $R+S$ is the effective resistance of the oscillatory circuit, then for the oscillations to be maintained or built up, the power supply from the valve must be equal to or greater than the $J^2(R+S)$ loss. This method of dealing with the problem has many practical advantages, and has been in use for some years. Hazeltine has described, in the "Proceedings" of the American Institute of Radio Engineers, the application of the method to various circuits, notably the circuit in which a condenser is connected across the grid inductance h . It is very well known that the author of this paper has had experience of many other circuits and applications of three electrode relays, and it is to be hoped that he may be able to give to the Society further papers on this same subject. In particular, a vector treatment of the De Forest ultraudion circuit would be of great interest, as this circuit is one which has presented very great difficulties when any attempts have been made to calculate the condition for instability.

Mr. J. NICOL asked if there was any lag between the voltage applied to the grid and the effect on the current in the valve.

Dr. D. OWEN said it was assumed that the action of the valve was an amplification of voltage. Actually what happened was a variation in the resistance of the valve. It seemed rather remarkable that this should be regarded as a voltage effect. He did not like Prof. Howe's idea of a negative resistance, as such a conception had no physical significance. A negative value of dV/dC was by no means the same thing as a negative value of V/C , which would be required before we could talk of a negative resistance. Did the author find it satisfactory to treat the quantity h_a as a constant?

Mr. F. E. SMITH thought the paper of great value. He agreed with Prof. Fortescue that a great amount of interesting work was still to be done in connection with these problems.

Capt. TURNER referred to a sentence occurring in the section dealing with a particular case: "It is noteworthy that . . . no resistance." This seemed to imply that an infinitesimal change in E would produce a finite change in the steady component of the anode current.

Dr. ECCLES, in reply, said that he did not think vector diagrams were ever used quantitatively. They were mainly used to derive a formula, and the scale of the vectors was immaterial. As regards lag, he was not aware of any definite knowledge on this point, but the fact that nowadays waves of 30,000,000 per second were obtained showed that the lag must be very small. He thought it was justifiable to assume it zero in slow circuits. The conception of the valve as a voltage amplifier seemed a difficulty; but if we vary the resistance of one part of a circuit containing a fixed E.M.F. it is clear that the P.D. on the remainder of the circuit will also vary; so that the varying resistance can be regarded as a source of varying E.M.F. applied to the remainder of the circuit. The quantity h_a was not constant. As regards Capt. Turner's point, he was referring here to a case in which there was no resistance in the inductance circuit.

A paper entitled "*A Small Direct-current Motor Using Thermionic Tubes instead of Sliding Contacts*," by Prof. W. H. ECCLES and Mr. F. W. JORDAN, was read by the latter.

In this motor the rotating part is an ebonite disc with iron teeth on its periphery, and the stationary part comprises two electromagnets with their poles close to two teeth. One electromagnet is connected to the grid of a thermionic relay, the other is included in the plate circuit. When during rotation a tooth passing the grid magnet induces a voltage in its winding the consequent transient increase of current through the other magnet causes this magnet to exert a pull on the tooth approaching it. We thus have a small motor without commutator or spark which may under no-load be driven up to a speed of 4000 to 6000 revs. per min. from the lighting supply.

Ordinary Meeting, February 28, 1919.

Prof. C. H. LEES, President, in the Chair.

A PAPER "*On Simplified Inductance Calculations, with Special Reference to Thick Coils*," by Mr. P. R. COURSEY, was read, in the absence of the author, by Mr. J. NICOL.

The method of calculation advocated in the paper is based on an extension of Nagaoka's formula for single layer coils, to include as well all ordinary forms of thick coils. Rosa's formula for thick coils is put into the same form as Nagaoka's, and its use enables a series of correction factors to be calculated for various coil thicknesses. By the aid of a single sheet of curves giving values of these correction factors the inductance of any form of coil likely to be met with in practice may be readily calculated, using only one simple standard formula for all cases. Reasonable accuracy is obtained even in the limiting example of a single turn of wire. The results arrived at agree well with other published charts, which are usually of more limited application, while the use of a single formula for all cases lessens the liability to error.

It is also shown that Raleigh and Niven's formula enables the calculation of the correction factors for very short coils to be carried out without having recourse to Nagaoka's more complicated expressions.

DISCUSSION.

Dr. ECCLES said that as the author had mentioned an abac given in the speaker's book on "Wireless Telegraphy," it was well to remark, first, that this abac was

deliberately made of its present range so as to provide an open scale for coils of the proportions used in practice. For the rare cases of coils outside the range of the abac very simple formulæ are available. Dr. Russell's formulæ were used in making the abac, because they seemed more convenient for the purpose than the results of Nagaoka, to which they were, of course, equivalent. By constructing new curves for dealing with coils of several layers the author has rendered a great service, and has opened easy paths though a forest of laborious theoretical calculation. Now that this has been done it will be much easier to compare the measured values obtained on actual coils with the calculated values, and so we shall be aided to accumulate experience of the effects of high frequency eddy currents on the inductance of coils.

Prof. HOWE agreed with Prof. Eccles' remark about the general utility of Mr. Coursey's investigation. The chief differences between the author's curves and those of the Bureau of Standards was that in the latter the ratio D/l and k , which was a function of D/l , were combined into a single function.

Mr. NICOL, in reply, referred to formulæ published in the *Electrician* by Mr. Coursey a few years ago, and considered that the step now taken, which resulted in restricting the values of k to between 0 and 1, combined with the general inclination of the curves to about 45 deg. with the axis, gave much greater convenience in reading.

A Demonstration of Some Acoustic Experiments in Connection with Whistles and Flutes was given by Dr. R. DUNSTAN.

Experiments were made with hollow spheres, cylinders, and cones with holes of various sizes and in various positions. Bernoulli's theorem, which gives the wave-length of the sound produced by a cylindrical pipe in terms of the length of the pipe and an end-correction depending on the diameter only, was shown to be quite inadequate for practical purposes, the pitch depending on many other factors, such as the wind pressure, the size and shape of the blow-hole, &c. Cylindrical flutes appear to require an end-correction which—within certain limits—is equal to D^2/d , where D is the diameter of the pipe and d the mean diameter of the mouth hole (which is often oval in shape). In the shortest flute experimented with, which was only half an inch long, Bernoulli's theorem would give the wave-length as two inches, whereas it was actually fourteen inches.

The conclusions drawn from the experiments are that in blowing across a hole in a hollow body a force existed on an elastic substance. The result is a "spring back," which produces an aerial throb, puff, or pulsation. The frequency of the pulsation is determined by relations between the dimensions of the instrument, the size of the hole, the wind pressure, &c. Any resulting sound has its wave-length determined by the frequency and not primarily by the dimensions of the instrument, as in the usual textbook treatment.

DISCUSSION.

Prof. BRAGG referred to Lord Rayleigh's work on open pipes and flasks, and said that since the internal pressure of the air would vary with the size of the aperture it was easily conceivable that a difference of pitch would result when a change was made in the size of the aperture.

Mr. F. J. W. WHIPPLE outlined Lord Rayleigh's explanation of the long wave-length of the notes obtained from a hollow sphere.

Mr. T. SMITH asked if the variation in pitch with the position of the hole along the cylinder had been fitted to a formula—for instance, was the change in pitch proportional to the square of the distance of the hole from the centre of the cylinder?

Mr. NICOL spoke of the end correction, and stated that students often applied the correction to the closed end of pipes, which was incorrect.

Mr. F. E. SMITH said the end correction was useful in electrical problems, and gave an illustration of the variation of D^2/d in an electrical case.

The PRESIDENT asked if there was much variation in the ratio D/d , and said he thought the formula was important if it could be verified over a wide range. He referred to Lord Rayleigh's experiments on flasks as closely analogous to those of Dr. Dunstan.

In reply, Dr. DUNSTAN stated that the range of D/d was not very large in the instruments he had used.

A Demonstration of a new Polariser was given by Mr. G. BRODSKY.

In the course of experiments with polarisers built of piles of glass plates disadvantages due to bulkiness of the apparatus and loss of light had to be overcome.

The idea occurred to him to place the pile of plates between two prisms of the same glass in such a manner as to—

- (a) Reduce the length of the polariser by one-half;
- (b) Utilise the full aperture of the pile; and
- (c) To get rid of all reflected light.

Results obtained with experimental prisms he showed were so good that they could be considered a very fair substitute for Nicol prisms of corresponding size, and the very small amount of light escaping through crossed prisms (which could be reduced further by additional plates) is for most purposes negligible.

There would be no difficulty in building such polarisers to any required size, as all the material consisted entirely of glass in unlimited quantities and at reasonable price, and it was hoped that this invention (Brit. Patent 221,906) would be used for many purposes.

Polarisers for directly transmitted light were hitherto very scarce and costly, so that many uses they could be put to remained undeveloped (such as stereoscopic cinematography).

The new polariser could also be adapted to advantage in microscopes, saccharimeters, optical pyrometers, &c., and used for optical benches in the lecture room.

Experiments with piles of glass plates showed a very large discrepancy between the calculated and observed angle for best extinction. Whatever the glass used, and whatever the quality of the surface, this discrepancy came consistently to some 10 deg., whereas thin microscope cover plates were found to be useless.

There seemed to be still an interesting field for investigation as to the conditions affecting the surface of glass plates used in polarisers.

DISCUSSION.

Mr. T. SMITH said it was difficult to discuss the merits of various forms of polariser, as many forms had been proposed and much was of a confidential character. He had been struck by the presence of two opposite tendencies in constructing such apparatus. In one group the optical portions of the apparatus were made large, and efforts were directed to increasing the size; in the other group, where the attainment of the same ultimate object was in view, these parts were made as small as possible.

The PRESIDENT asked if it was not possible to get equally good results without prisms by reflection only. He thought prisms made the arrangement complicated.

Mr. BRODSKY, in reply, explained that he agreed with the remarks about reflection, but that his efforts were confined to transmission effects for a particular purpose.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, March 5, 1919.

Dr. SAMUEL RIDEAL, President, in the Chair.

A CERTIFICATE was read for the first time in favour of Mr. Madanlal Jekisandas Gajjar, M.A. (Bombay), and Mr. James Sorley, F.I.C.

Certificates were read for the second time in favour of Messrs. Robert Odell Bishop, A.I.C.; Hubert William Bywaters, D.Sc., F.I.C., Ph.D.; B. S. Evans, M.C.,

B.Sc.Lond., F.I.C.; F. S. Fowweather, M.Sc., A.I.C.; Robert Atkinson Oddy; W. B. Pollard; Charles Kenneth Tinkler, D.Sc., F.I.C.

Mr. Cecil William Wood was elected a Member of the Society.

The following papers were read:—

"*Approximate Method of Analysis of Sausages and Meat Paste.*" By GEO. STUBBS, O.B.E., F.I.C., and A. MORE, A.R.C.S., F.I.C.

The determination of moisture, fat, proteins, and ash is carried out in the usual manner, and the proportion of carbohydrates taken by difference. The estimation of lean meat is based on the absence of carbohydrates in meat and the amount of proteins in the cereal products used as fillers.

"*Method for the Determination of Small Quantities of Acetone, Alcohol, and Benzene in the Air.*" By Major S. ELLIOTT, B.Sc., F.I.C., and Capt. J. DALTON, M.C.

A measured quantity of the air is drawn through suitable apparatus, the vapours being absorbed simultaneously as follows:—The acetone in alkaline iodine solution and the excess of iodine titrated with thiosulphate. The alcohol in dilute chromic acid and, after oxidation to acetic acid, the excess of chromic acid is titrated with iodine. The benzene in a mixture of conc. sulphuric acid and fuming nitric acid, converted into dinitro-benzene, and after extraction with ether, reduced by a known excess of stannous chloride and the excess of the last reagent titrated with iodine.

"*Analysis of Sausages, Meat Pastes, and Army Rations.*" By A. W. STOKES, F.I.C.

The Food Control authorities limited the percentage of meat which might be contained in sausages to be sold at a given price, but did not limit the quantities of bread, water, and fat. The desirability of limiting the quantities of water, bread, and fat was shown by a particular sample which contained about equal parts of added water, bread, fat, and meat. Since meat contains 70 per cent of water and bread 40 per cent, no added water should be allowed. In the United States the use of bread in sausages is prohibited, and, as the bread is often soaked in water before use, thereby increasing the percentage in the finished product, the author points out that this prohibition might with advantage be enforced in England.

INSTITUTE OF CHEMISTRY.

THE London and South-Eastern Section of the Institute of Chemistry was formed at a meeting held at 30, Russell Square, on March 14.

Sir HERBERT JACKSON, President, in opening the proceedings, said that the Local Sections of the Institute recently formed in various parts of the country had already demonstrated their usefulness, and were taking an active part in assisting the Council in promoting the interests of the profession of chemistry. The Council desired that the Local Sections should have a free hand in the conduct of their business. The President, therefore, called upon the members to elect a Chairman for the meeting.

Dr. BERNARD DYER having been elected to the chair, the Section was declared duly formed.

A Committee was elected as follows:—Mr. C. T. Abell, Dr. O. L. Brady, Mr. A. J. Chapman, Miss E. M. Chatt, Dr. Bernard Dyer, Mr. A. V. Elsdon, Mr. Norman Evers, Mr. J. A. Gardner, Mr. C. S. Garland, Dr. W. H. Gibson, Mr. W. H. Harrison, Mr. E. M. Hawkins, Prof. J. W. Hinchlev, Prof. P. H. Kirkaldy, Mr. E. H. Lees, Mr. T. Macara, Mr. W. A. C. Newman, Mr. F. M. Potter, Mr. F. M. Ray, and Mr. J. Miln Thomson.

Mr. William Bacon was appointed Hon. Secretary, *pro tem.*

The draft rules for Local Sections were provisionally adopted, and a general discussion ensued on the proposed revision of the By-Laws for the election of the Council of the Institute.

CORRESPONDENCE.

ATOMIC STRUCTURE AND CHEMICAL AFFINITY.

To the Editor of the Chemical News.

SIR,—Referring to my article, entitled as above, in last week's issue of the CHEMICAL NEWS, may I claim a little more space to correct two mathematical errors?

Page 145, left-hand column, bottom line, "10-2 cm." should read 10-24 cm.

Page 149, left-hand column, first figures in table, "10-6" should read 10⁶.

It will be seen that by making this latter correction the gradation of the wave-lengths is as it should be.—I am, &c.,

F. H. L.

DYEING EXPERIMENT.

To the Editor of the Chemical News.

SIR,—Turning over the pages of my laboratory notebooks for the late sixties, I find the following:—"Take half a grm. of a mixture in powder of potassium methyl sulphate and potassium iodide, tint slightly with rosaniline, moisten with glycerol, and warm carefully over the flame; Hofmann's violet is formed. On addition of water, silk or wool can be dyed in the solution. The experiment would serve for lecture demonstration when dealing with aniline dyes. Glycerol retains the CH₃I."

The enclosed was dyed by this means. [The strip of silk accompanying was dyed a pleasing shade of violet.—ED.]—I am, &c.,

EXPERIMENTER.

MISCELLANEOUS.

Institute of Chemistry.—At a meeting of Fellows and Associates of the Institute of Chemistry held at Milburn House Café, Newcastle-upon-Tyne, it was decided to form a Local (Newcastle and North-East Coast) Section. Prof. P. Phillips Bedson presided, and the Registrar of the Institute was also present. A Committee was appointed consisting of Prof. Bedson, Dr. J. T. Dunn, Prof. Henry Louis, Mr. R. A. Moore, Mr. C. H. Ridsdale, and Mr. Thomas Wallace. The Committee was empowered to add three to their number, and Dr. Dunn was appointed Hon. Secretary *pro tem.* The draft rules for Local Sections of the Institute were discussed and approved, as was also the suggested scheme for the revision of the By-laws for the election of the Council of the Institute.

MEETINGS FOR THE WEEK

MONDAY, 7th.—Royal Institution, 5. (General Meeting).

— | Royal Society of Arts, 4.30. (Cantor Lectures). "Problems of Food and their connection with Our Economic Policy," by Prof. H. E. Armstrong.

— | Society of Chemical Industry, 8. "Drying by Heat in conjunction with Mechanical Agitation and Spreading," by E. A. Allott. "Estimation of Carbon Disulphide—a Critical Examination of the various Methods usually Employed," by P. E. Spielmann and F. B. Jones. "Estimation of Thiophene," by P. E. Spielmann and S. P. Schotz. "Estimation of 'Free Carbon' in Tar and Pitch," by P. E. Spielmann and H. Wood.

TUESDAY, 8th.—Royal Institution, 3. "British Ethnology—The People of Wales," by Prof. A. Keith.

WEDNESDAY, 9th.—Royal Society of Arts, 4.30. "Housing and Infant Mortality," by Dr. L. E. Hill.

THURSDAY, 10th.—Royal Institution, 3. "Colloidal Matter and its Properties," by Prof. A. Findlay.

— | Institution of Electrical Engineers, 6. "Notes on Surface Condensing Plants, with Special Reference to the Requirements of Large Power Stations," by R. J. Kaula.

FRIDAY, 11th.—Royal Institution, 5.30. "Piezo Electricity and its Applications," by Prof. Sir J. J. Thomson.

SATURDAY, 12th.—Royal Institution, 3. "Spectrum Analysis and its Application to Atomic Structure," by Prof. Sir J. J. Thomson, O.M.

SIR WILLIAM CROOKES.

THE death of Sir William Crookes, which took place on Friday morning last, has been announced the world over, and full accounts of his labours and attainments have been published. There is no need for repetition in these pages; but a few words from one who for more than half a lifetime has been closely associated with him in his scientific work may not be considered out of place.

Sir William Crookes was a remarkable man: scientific work was his chief object in life; research and the progress of science his one interest.

His energy and patience were remarkable, both in success and failure—for of failures there were many about which the world knew nothing.

There were two terms that he called "bad words," and would not allow in the laboratory—one was "cannot," the other "near enough."

He was a hard worker; day in day out was filled with labour; and one of his common sayings was that a man could not be really happy unless he had just a little more to do each day than he could possibly finish.

The work of the CHEMICAL NEWS was one of his few recreations, and the paper was under his personal control from the day of its foundation in 1859 until within a few weeks of his death.

The death of Lady Crookes, which took place in May, 1916, deprived him of his one companion, and undoubtedly hastened his death. With her he lost his main interest in life, and, although he bravely fought on, it was plain to see that he would never be the same again. Gradually his strength gave way, and the writer, watching him, saw a daily added feebleness; but there was never a murmur or word of complaint, always the same kindly greeting and pleasant smile, until physical weakness gained the upper hand and he passed quietly away in the early hours of the morning.

"And so familiar landmarks disappear, old memories fade away, and all the busy actors in life's theatre vanish, and those who are left are those who are to be pitied."

THE CHEMICAL NEWS

VOL. CXVIII., No. 3078.

A STUDY OF THE PREPARATION OF CERTAIN ORGANIC SALTS OF TELLURIUM.*

By AARON M. HAGEMAN.

In an investigation described elsewhere (*Journ. Am. Chem. Soc.*, 1919, xli., 300) it was necessary to secure solutions of tellurium in a number of non-aqueous solvents. This led to an investigation of certain organic salts of tellurium, since, in many cases, combinations of a metal with an organic acid radical are more likely to be dissolved by organic liquids than are inorganic salts. Although tellurium dioxide is chiefly acid in character, there are numerous cases where it shows specific basic tendencies. This suggested a general method for the preparation of organic salts of tellurium, namely, the treatment of tellurium dioxide with the free organic acid. In some cases this proved to be a satisfactory method of prepara-

tion, while in numerous other cases a chemical union could not be brought about by this means. This was especially true where the acid character of the organic acid was unusually weak.

Experimental.

Tellurium Acid Tartrate.—It was known to Berzelius (*Pogg. Ann.*, 1826, viii., 411) that tellurium dioxide could be dissolved in tartaric acid and a salt separated out in which tellurium acted as a base. Becker further studied this reaction and reported (*Ann.*, 1876, clxxx., 257) that if a solution of tellurium dioxide in tartaric acid was allowed to evaporate spontaneously in the air, long, radiating, colourless crystals separated out, which his analysis showed to be tellurium acid tartrate, $\text{Te}(\text{HC}_4\text{H}_4\text{O}_6)_4$. Becker (*loc. cit.*) states it is very difficult to separate these crystals from the tartaric acid itself.

In the present work the preparation of the salt consisted in treating a solution of tartaric acid, saturated at 20° C., with an excess of purified tellurium dioxide which had been ground to pass a 200-mesh sieve. The mixture was contained in an Erlenmeyer flask fitted with a one-holed rubber stopper in order to minimise evaporation and was heated in a sand-bath at a temperature of 70° C. At the end of three days, reaction had taken place, as evidenced by a decrease in the quantity of the dioxide, while a small amount of elementary tellurium had separated out.

After prolonged heating at this temperature, a portion of the liquid was filtered and the materials in solution

* Abstract of part of a thesis submitted to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy. From the *Journal of the American Chemical Society*, xli., No. 3.

allowed to crystallise. After being freed from the mother-liquor as completely as possible by pressing between filter-paper, an analysis of the colourless crystals showed them to contain 5.60 per cent tellurium. The formula $\text{Te}(\text{HC}_4\text{H}_4\text{O}_6)_4$ requires 17.62 per cent tellurium. The flask containing the dioxide and tartaric acid was heated again for two months longer at 70°C . and crystallisation allowed to take place at room temperature, since if the solution is boiled the tellurium will slowly but completely precipitate as the element. The crystals separating out proved to contain 16.38 per cent tellurium, which is approximately the theoretical percentage required.

The reaction taking place between tellurium dioxide and tartaric acid may be summarised as follows:—A strong solution of tartaric acid slowly dissolves tellurium dioxide with the formation of tellurium acid tartrate. Inasmuch as the solubility of the free acid and newly formed salt are very nearly the same, it is impossible to separate them by this means. It consequently becomes necessary to continue the reaction to completion. Heating accelerates the reaction, but a boiling temperature must be avoided as it will cause the separation of tellurium in the elementary form.

Tellurium Acid Citrate.—Since tellurium was able to replace one of the two hydrogen atoms of the dibasic tartaric acid, it was interesting to determine the number of hydrogen atoms this element was able to replace in a tribasic organic acid. Preliminary experiments showed tellurium dioxide to be slowly dissolved by citric acid. Tellurium dioxide and a solution of citric acid were heated together for one month in a manner similar to the procedure just described. During this time no elementary tellurium was set free as in the case with tartaric acid. Crystals separating out from the supernatant liquid after concentration on a hot plate were of two different types. They consisted of large, colourless crystals which were recognised as crystals of citric acid, and some small white opaque crystals. An analysis of the latter showed a content of 9.73 per cent tellurium. By dissolving the small, white, opaque crystals in distilled water and re-crystallising, it was found that similar crystals separated first and others of citric acid later. An analysis of the former showed them to contain 21.25 per cent tellurium. Fractional crystallisation was therefore continued. The results of the analyses carried out with each fraction of crystals are arranged in the accompanying table:—

Fraction.	Wt. sample. Gm.	Wt. Te found. Gm.	Te. Per cent.
1. . .	0.6133	0.0509	9.73
2. . .	0.5270	0.1120	21.25
3. . .	0.5793	0.1394	24.07
4. . .	0.5439	0.1333	24.50
5. . .	0.3264	0.0819	25.09

Since the percentage of tellurium required for the formula $\text{Te}(\text{HC}_6\text{H}_5\text{O}_7)_2$ is 25.10 per cent, it appears that this compound is produced by the action of citric acid on tellurium dioxide. Tellurium acid citrate may be described as a white, opaque, finely crystalline compound which tends to separate in small, radiating clusters. In comparing its preparation with that of the acid tartrate, it is of interest to note that its solution in water will withstand boiling temperatures without reduction to the element. Its solubility is sufficiently less than that of citric acid to permit its complete separation from the free acid.

Tellurium Oxalate.—If tellurium dioxide is heated with a saturated solution of oxalic acid, a certain amount of tellurium is held in solution as shown by tests for the element. If such a solution is allowed to crystallise spontaneously in the air, a mixture of crystals of the dioxide and acid separate. There seems, therefore, to be no compound existing between tellurium and the oxalic acid radical. Klein obtained similar results when he attempted to prepare a double oxalate of potassium and tellurium (*Ann. Chim. Phys.*, 1887 [6], x., 108; *Bull. Soc. Chim.*, xlv., 714).

Tellurium Succinate.—A solution of succinic acid was heated with finely divided tellurium dioxide for three months. At no time did a portion of the filtered solution respond to a test for tellurium. There is apparently no action between tellurium dioxide and succinic acid.

Tellurium Dioxide and Certain Other Organic Acids.—An excess of tellurium dioxide was also heated with concentrated solutions of malic, gallic, and lactic acids for long periods of time. All of these acids slowly dissolved small amounts of tellurium dioxide. In the case of malic and gallic acids, crystals could be obtained which contained small amounts of tellurium, but it was impossible to separate the tellurium containing substances from the free acid. The solution obtained in lactic acid failed to yield any crystals after concentration by various methods. It was evident that if a definite compound was formed it was soluble in the liquid lactic acid. In none of these cases was there a separation of elementary tellurium during the long periods of heating, as was the case with tartaric acid.

Klein (*loc. cit.*) had similar experience with tellurium dioxide and phosphoric acid. A reaction between these two compounds could be recognised. He states, however, he was entirely unable to separate out a definite compound containing tellurium and phosphoric acid.

Tellurium Oleate.—Tellurium tetrachloride proved to be easily soluble in anhydrous benzene. Kahlenberg (*Journ. Phys. Chem.*, 1902, vi., 1) has shown that if a solution of copper oleate in benzene is treated with a metallic chloride dissolved in benzene, a brown precipitate of anhydrous copper chloride is produced with the metallic oleate. This suggested a means of preparation of tellurium oleate and certain other compounds of tellurium with the higher fatty acids.

A solution of purified copper oleate in anhydrous benzene was treated with an excess of a solution of tellurium tetrachloride in benzene. A precipitate of brown anhydrous copper chloride immediately formed. The precipitate was gelatinous and extremely difficult to filter. Before filtration could be effected, a purple colour developed in the solution and in the precipitate. This indicated that if tellurium oleate had originally been formed, it rapidly dissociated into colloidal tellurium and free oleic acid.

Various attempts were made to salt out an oleate of tellurium from the solution immediately after precipitation. As "salting out" agents, water, as well as organic liquids in which the metallic oleates are usually insoluble, were used, but the tellurium always separated in the elementary form before a definite compound could be obtained.

Final attempts were made by using molecular proportions of the two reagents dissolved in benzene. The benzene was carefully removed at a temperature not exceeding 65°C . The remaining black residue consisted of a mixture of free oleic acid, copper chloride, and elementary tellurium.

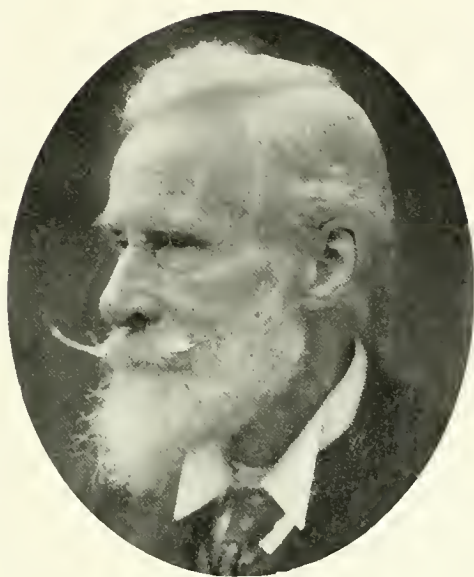
It is therefore evident that these methods do not offer a means of preparation of this compound. Results show that tellurium oleate is probably produced, but tellurium and oleic acid are so weakly basic and acid, respectively, that the compound immediately dissociates into elementary tellurium and free oleic acid.

A number of similar experiments were carried out with copper stearate solutions but with identical results.

Summary.

1. A detailed method for the preparation of tellurium acid tartrate has been given. It was found that this salt cannot be separated from tartaric acid by crystallisation. This is contrary to the findings of Becker.

2. Tellurium acid citrate— $\text{Te}(\text{HC}_6\text{H}_5\text{O}_7)_2$, is produced by the action of a concentrated solution of citric acid on tellurium dioxide. This salt crystallises in white, opaque, radiating crystals. It differs from the acid tartrate in that its solutions will withstand boiling temperatures without



SIR WILLIAM CROOKES, O.M., F.R.S.,
Born June, 1832. Died April, 1919.

reduction and its solubility is sufficiently less than that of the free acid to permit purification by fractional crystallisation.

3. Succinic acid does not attack tellurium dioxide.

4. Oxalic, lactic, malic, and gallic acids hold appreciable amounts of tellurium dioxide in solution. It was impossible to separate a crystalline compound of tellurium with any of these acids.

5. The existence of an oleate or stearate of tellurium has been shown to be doubtful.

The author takes pleasure in acknowledging his obligation to Prof. Victor Lenher, at whose suggestion and under whose guidance and inspiration the work of this and the preceding paper (which will appear later) has been carried out.

PHYSICAL CHEMISTRY AND ITS BEARING ON THE CHEMICAL AND ALLIED INDUSTRIES.*

By Prof. JAMES C. PHILIP, O.B.E., M.A., Ph.D., D.Sc.

(Continued from p. 161).

THE very marked falling off in the yield of sulphur trioxide with rising temperature is in harmony with the well known physico-chemical principle associated with the name of Le Chatelier, viz., that if any change in the external conditions (pressure and temperature) is imposed on any system in equilibrium, then the equilibrium shifts in such a direction as to meet and partially neutralise the change in question.

If, for example, the temperature of a closed vessel containing only water and water-vapour is raised, some of the water will evaporate until the vapour pressure has risen to the value appropriate to the higher temperature. Evaporation, however, is accompanied by absorption of heat, and the equilibrium between water and water-vapour shifts therefore with rise of temperature in that direction which involves a partial neutralisation of the heat communicated from the outside.

So with any reversible chemical reaction, if the temperature of the equilibrium mixture is raised, the position of equilibrium shifts in that direction which involves absorption of heat. Now, the formation of sulphur trioxide from sulphur dioxide and oxygen is an exothermic process; i.e., the change $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$ is accompanied by the evolution of heat, and it therefore follows that the reverse process—the dissociation of the trioxide—involves absorption of heat. Rise of temperature accordingly favours the formation of the system sulphur dioxide + oxygen at the expense of the sulphur trioxide.

The influence of temperature on the equilibrium constant K of a reaction, and its relation to the heat effect of the reaction is expressed in the thermodynamic equation—

$$\frac{d(\log_e K)}{dT} = -\frac{Q}{RT^2},$$

where Q is the quantity of heat liberated when the reaction goes completely from left to right at the absolute temperature T , and R is the well-known gas constant. It appears that the value of Q for the reaction $2\text{SO}_3 = 2\text{SO}_2 + \text{O}_2$ is a linear function of the temperature, and may be represented by the equation $Q = -47,300 + 4T$. If this value of Q is put in the foregoing thermodynamic equation, and the latter is then integrated, a formula is obtained which expresses the variation of K with the temperature, viz.:—

$$\log_{10} K = -\frac{10373}{T} - 2.22 \log_{10} T + 14.585.$$

The values of K given by this equation are in close agreement with the experimental figures.

The Le Chatelier principle referred to above makes it

possible to predict the effect of increasing the pressure on any equilibrium system at constant temperature. If, for example, ice and liquid water are in equilibrium at 0°C ., and a bigger pressure is applied, the system meets this by shrinking; i.e., the equilibrium shifts so as to increase the proportion of the denser constituent (liquid water) at the expense of the lighter (ice). Similarly, with any reversible chemical reaction at a given temperature, increase of pressure favours the formation of the system occupying the smaller volume, and the equilibrium accordingly shifts in that sense.

In the equilibrium represented by $2\text{SO}_3 \rightleftharpoons 2\text{SO}_2 + \text{O}_2$,

the number of molecules on the left being two, that on the right three, it is clear that the sulphur trioxide occupies a smaller volume than the sulphur dioxide and oxygen from which it is formed. Hence increase of pressure at any temperature would lead to a greater percentage conversion of the dioxide into the trioxide. If the maximum yield of sulphur trioxide obtainable at the ordinary pressure and at all temperatures within the possible working range were comparatively low, then it might be desirable, even on the manufacturing scale, to carry out the contact process under pressure. Since, however, that contingency does not arise, the question of operating under pressure does not present itself in any practically urgent shape.

The law of mass action, then, coupled with the principles of thermodynamics, leads to a complete quantitative presentation of the equilibrium between sulphur trioxide, sulphur dioxide, and oxygen, as it exists over a fairly wide range of temperature, and if the yield were the only factor to be considered in the contact process, it is plain that the lower the working temperature the better. The manufacturer, however, has to take another factor into account, and that is the time required at each temperature for the establishment of the equilibrium. The velocity of chemical reactions, as shown by innumerable physico-chemical investigations, has a very big temperature coefficient, and as a rule is doubled or trebled for a rise of 10°C . The contact process is no exception to this rule, and the rate at which sulphur dioxide and oxygen combine to form sulphur trioxide in presence of a catalyst increases very rapidly with rising temperature.

The practical question is whether, at those temperatures for which the yield approaches 100 per cent, the reaction proceeds to equilibrium in a reasonably short time. Clearly the manufacturer might prefer a somewhat lower yield of the trioxide, combined with a greater rate of reaction, than an almost quantitative yield with a slow reaction and the extra costs which this would involve. Such a question must manifestly be decided in favour of those working conditions which give the best economic return.

Fortunately, in the case of the contact process, it is possible to operate with satisfactory speed even at temperatures as low as $400-500^\circ$, where the percentage yield is still very high. This possibility is due to the fact that platinum, in one form or another, is such an efficient catalyst of the reaction between sulphur dioxide and oxygen. Other and less efficient catalysts, such as the ferric oxide obtained by roasting pyrites, can be and are employed, but the establishment of equilibrium at $400-500^\circ$ in such cases would be a very slow and uneconomical process. When ferric oxide is used as catalyst in the contact process, the balance between yield and rate of change is struck by working at about 600° . Not until this temperature is reached does the reaction in presence of ferric oxide become reasonably rapid. The yield under these conditions goes down to 60–70 per cent, but against this may be put the fact that this is achieved by the use of a cheap contact substance. When ferric oxide is used as the catalyst, as in the Mannheim process, the unchanged sulphur dioxide may, after removal of the trioxide by absorption, be passed into a second converter in which a platinum catalyst is employed.

* Canton Lecture (I.). Delivered before the Royal Society of Arts, December 2, 1918. From the *Proceedings of the Royal Society of Arts*, xvii., No. 3450.

Another important technical gas reaction which is of peculiar interest from the standpoint of these lectures, and has been of great significance in connection with the war, is the synthesis of ammonia from nitrogen and hydrogen. In the case of the sulphuric acid contact process, the technical development was largely independent of and anterior to the application of physico-chemical principles, however valuable these may now be in formulating the influence of varying conditions and in giving quantitative expression to the possibilities of the process. In the synthesis of ammonia, on the other hand, the physico-chemical investigation came first, and the large-scale process now operated is the direct outcome and development of work carried out on purely scientific lines.

It has long been known that when electric sparks are passed through ammonia gas for some time it splits up into the constituent elements, but Deville pointed out about fifty years ago that even after prolonged sparking there was still a trace of ammonia left, as was proved by the faint white cloud formed when a little hydrogen chloride gas was mixed with the decomposition products. Deville further succeeded in showing that a minute quantity of ammonia is produced when a mixture of nitrogen and hydrogen is passed through a heated tube.

The real recognition of the decomposition of ammonia as a reversible reaction came, however, much later, and the application of the principles of chemical equilibrium to this case belongs to quite a recent period. In 1905 Haber showed that if ammonia is passed over finely divided iron at a high temperature (about 1000° C.) a small quantity of the gas escapes decomposition; and, further, if the residual nitrogen and hydrogen, now freed from ammonia, is passed over finely-divided iron at the same temperature as before, fresh ammonia is generated, the quantity being practically equal to that which escaped decomposition in the first instance. It is clear, therefore, that the reaction is a reversible one, and may accordingly

be written $N_2 + 3H_2 \rightleftharpoons 2NH_3$, although there is no doubt that at 1000° C. and the ordinary pressure the equilibrium position lies almost at the system represented by the left-hand side of this equation.

It is instructive and, as it turns out, of the highest practical significance, to study the influence of changing pressure and temperature on the ammonia equilibrium. In this investigation Le Chatelier's principle is again a trustworthy guide. It has already been stated that in any reversible chemical reaction which has reached equilibrium an increase of pressure at constant temperature favours the formation of the system occupying the smaller volume, and shifts the equilibrium in that sense. The application of this

theorem to the ammonia equilibrium $N_2 + 3H_2 \rightleftharpoons 2NH_3$, leads to the conclusion that the equilibrium mixture at any temperature will contain a greater proportion of ammonia when the pressure is high than when it is low. If the object is to produce ammonia by the union of hydrogen and nitrogen, then the yield will be increased by working under high pressures.

A more definite formulation of this pressure effect is possible when we turn to the equilibrium constant and express it, not in terms of the equilibrium concentrations of nitrogen, hydrogen, and ammonia, but in terms of their equilibrium partial pressures, p_{N_2} , p_{H_2} , and p_{NH_3} . On this basis

$$\frac{p_{NH_3}}{p_{N_2} \cdot p_{H_2}^3} = \text{const. at a given temperature, or alternatively,}$$

$$K = \frac{p_{NH_3}}{p_{N_2} \cdot p_{H_2}^3}. \text{ Now, at b.l. temperatures } p_{NH_3} \text{ is}$$

known to be small compared with p_{N_2} or p_{H_2} , and so long as this condition holds no great error is involved in

writing $p_{N_2} + p_{H_2} = P$, where P is the total pressure of the three gases. Further, where the nitrogen and hydrogen have been taken in the volume proportion 1 : 3, $p_{H_2} = 3p_{N_2}$. When these relationships are coupled with the equation for the equilibrium constant it follows that $p_{NH_3} = 0.325 K \times P^2$ —that is, the partial pressure of the ammonia in the equilibrium mixture is, for low concentrations of ammonia, proportional to the square of the total pressure.

The percentage of ammonia by volume (x) in the equilibrium mixture will be given by—

$$x = \frac{p_{NH_3}}{P} \times 100 = 0.325 K \times P,$$

and it is therefore to be expected that x will increase approximately in proportion to the total pressure of the reaction mixture. This prediction is confirmed by experiments in which Haber showed, for example, that the volume percentage of ammonia in the equilibrium mixture at 800° and a pressure of one atmosphere was about 0.012, whereas under a pressure of thirty atmospheres at the same temperature the percentage was 0.34; i.e., nearly thirty times as great.

The approximate proportionality between the volume percentage of ammonia in the equilibrium mixture and the total pressure is further emphasised by the figures given below (Haber), which show the exactly calculated influence of high pressures on the position of equilibrium at different temperatures. It will be observed, on reference to these figures, that the proportionality between the percentage of ammonia and the pressure is most exact where the values of the former are low. Where these values become appreciable their increase is somewhat less than proportional to the rise of pressure.

At an early stage in the experimental investigation it was recognised that a rise of temperature was inimical to the conversion of nitrogen and hydrogen into ammonia, but this is only what could be foreseen on the basis of Le Chatelier's theorem. For the combination of nitrogen and hydrogen to form ammonia is accompanied by the evolution of heat, and since rise of temperature invariably shifts an equilibrium in the direction which involves absorption of heat, it follows that the percentage of ammonia obtainable from the two gases diminishes as the temperature rises.

This may be put more definitely with the help of the thermodynamic equation—

$$\frac{d \log_e K}{dT} = - \frac{Q}{RT^2},$$

already quoted in connection with the sulphur trioxide equilibrium. If the relation between specific heat and temperature is known for each of the gases concerned in a gaseous reaction, the variation of the heat effect Q can be formulated, for, according to Kirchhoff's theorem,

$$\frac{dQ}{dt} = C_1 - 2, \text{ where } C_1 \text{ is the sum of the molecular}$$

specific heats of the reacting substances at constant pressure, and C_2 is the corresponding quantity for the resulting products. In the case of the ammonia reaction C_1 is the true specific heat at constant pressure of a mixture of $\frac{1}{2}$ gram. molecule of nitrogen + $\frac{3}{2}$ gram. molecule of hydrogen, and has been found to be $13.47 + 0.00164 t$, where t is temperature centigrade. The quantity C_2 , on the other hand, is the true specific heat at constant pressure for 1 gram. molecule of ammonia, and is given by the equation $C_2 = 8.62 + 0.0035 t + 5.1 \times 10^{-6} t^2$. If these expressions

are inserted in the Kirchhoff formula $\frac{dQ}{dt} = C_1 - C_2$, and

this is integrated, then—

$$Q = Q_0 + 4.85t - 0.00093t^2 - 1.7 \times 10^{-6}t^3 \text{ gram. calories.}$$

The constant Q_0 represents the heat evolved in the reaction $\frac{1}{2}(N_2 + 3H_2) = NH_3$ at 0° C., and has been found to be 10950 cal., so that the heat effect of the foregoing reaction at $t^\circ C.$ is given by—

$$Q = 10950 + 4.85t - 0.00093t^2 - 1.7 \times 10^{-6}t^3.$$

If this expression for the heat of reaction is put in the equation—

$$d(\log_e K) = - \frac{Q}{RT^2}$$

and the latter is then integrated, a formula is finally obtained which represents the equilibrium constant of the ammonia reaction as a function of temperature. The formula so found by Haber is—

$$\log_{10} K = \frac{2098}{T} - 2.5088$$

$$\log_{10} T - 0.0001006 T + 0.186 \times 10^{-6} T^2 + 2.1$$

The values of K calculated in this way are in remarkably good agreement with the experimental determinations of the ammonia equilibrium, as is shown, for example, by the measurements made at thirty atmospheres pressures and various temperatures:—

$^{\circ}\text{C}.$	$K \times 10^4$ found.	$K \times 10^4$ calc.
561°	21.3	21.5
620°	12.6	12.7
700°	6.80	6.88
722°	5.82	5.92
801°	3.56	3.00
901°	2.13	2.11
952°	1.68	1.66

To be continued).

THE PRODUCTION OF NITROGEN COMPOUNDS.*

By JACK P. MONTGOMERY, Department Chemistry
and Chemical Engineering, University of Alabama.

(Concluded from p. 164).

Production now Normal.

IT is estimated that the production of nitrogen compounds by the two ammonia fixation processes and from the distillation of coal have now reached the annual rate, calculated on the comparative basis of nitrogen and not differentiating the various compounds, for the synthetic processes 100,000 tons, coal distillation 300,000 tons, and cyanamide process 325,000 tons. This is about equal to the total annual amount of nitrogen used in the world prior to 1914.

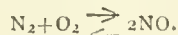
Nitric acid is now made by three methods, from sodium nitrate by distillation with sulphuric acid, by the oxidation of ammonia, and by the direct oxidation of atmospheric nitrogen. The strongest nitric acid of commerce is made by distilling sodium nitrate with sulphuric acid. In fact this is the only convenient or workable method for making the concentrated acid suitable for nitrating. The other methods of making nitric acid give a weak product which must be concentrated. It is far cheaper to import the sodium nitrate from Chile and make the concentrated acid directly from it than to concentrate the dilute acid made by the other two processes. Until a very few years ago, certainly prior to the beginning of the present century, the nitrate beds of Chile were more important than all the other sources of nitrogen combined, and that source is still of greater importance than any other one source of nitrogen compounds. In 1914, before the beginning of the war, the production of Chilean nitrate, including that used by Germany, was at the annual rate of 3,000,000 tons, and in 1918, with none going to Germany, the production was 3,700,000. This sodium nitrate was used to a great extent directly as a fertiliser. It was also used, and particularly during the war, as a source of nitric acid for use in the manufacture of munitions. Although vast quantities of nitrates may be made from atmospheric

nitrogen and from the oxidation of ammonia, sodium nitrate may be expected to maintain its importance for many years. It will be used primarily as the source of the concentrated nitric acid and will not lose its importance as a fertiliser. The U. S. Department of Agriculture last winter, in spite of the fact that the war was being prosecuted, made arrangements to sell to the farmers of the country a great volume of Chilean nitrate, and during the present winter even more is to be imported for this purpose. This is an index of the importance of sodium nitrate as a fertiliser and evidence that it is not in danger of being forced into obscurity.

Direct Oxidation of Nitrogen.

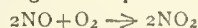
The direct oxidation of the nitrogen of the air in the manufacture of nitric acid constitutes the remaining method for the fixation of atmospheric nitrogen to be described. As long ago as 1785 Cavendish noted that oxides of nitrogen could be obtained by passing an electric spark through air in an inclosed space. It is a matter of record that he made dilute nitric acid by this process. In 1901 Bradley and Lovejoy established at Niagara Falls a factory using this method of making nitric acid from atmospheric nitrogen. Their apparatus consisted of two concentric cylinders carrying platinum electrodes regularly spaced on the inside surface of the outer cylinder and on the outside surface of the inner cylinder. The apparatus was so arranged that as the inner cylinder revolved arcs were sprung between adjacent electrodes on the two cylinders, and as the electrodes moved apart the arcs were strung out until they were extinguished. Air was passed through the space in which the arcs were formed and some nitric oxide was produced. This was oxidised further to nitrogen peroxide, which was absorbed in towers, forming nitric acid, with water. This apparatus did not prove a commercial success, but paved the way for other attempts.

Birkeland and Eyde met with better success in Norway and their work was improved upon by Schönher and by Paulding. In each of these processes there are devices to cause the production of large arcs with large surfaces through which the air is forced at a regular rate. The first reaction is represented by the equation—

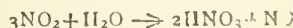


It was formerly thought that the nitric oxide was produced by a thermal effect, but it has been recently shown that the forward action in the above equilibrium is induced by the electrical effect, while the backward action, involving the decomposition of the nitric oxide, is thermal. A study of the equilibrium conditions in the above system revealed the fact that if the gases were not cooled with great rapidity the backward action is fast enough to undo the work of the arc to such an extent that the process could not be a success. This, in fact, was the key to the solution of the whole problem, and the achievements of Birkeland and Eyde and their associates were due in large measure to the provisions made for rapidly cooling the mixture issuing from the furnaces in which the air had passing through the arcs. This cooling is accomplished by passing the gases through the tubes of specially designed boilers in which the excess heat was used in the production of steam. The mixed gases issuing from the boiler tubes are at about 150° C. and at that temperature the decomposition of the nitric oxide is negligible. Under these conditions of rapid cooling the nitric oxide content of the gases coming from the arc furnaces may be worked up to 1.5 per cent.

On further cooling the nitric oxide takes up oxygen from the air according to the equation—



By interaction with water nitric acid is formed and follows:—



This interaction occurs in absorption towers and the product is dilute nitric acid, which may be neutralised with lime to form calcium nitrate, which in turn is used as a fertiliser or as a source of concentrated nitric acid.

Cheap Power not Necessary.

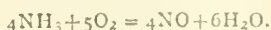
It is popularly believed that the arc process for the direct production of nitric acid from atmospheric nitrogen can be profitably carried out only where there is cheap and abundant water power, as is the case in Norway, but, as was pointed out above, the success of the process depends rather upon attention paid to the equilibrium conditions. This process is admirably adapted for use wherever there is a source of current with an off peak load for some hours each day. It takes very little time to get the process under way, and it has been suggested that small units should be established at a number of hydro-electric power plants where for a part of the day the power is not being developed or used. Another interesting development or extension of this process may be expected in connection with by-product coke plants which have a large volume of gas going to waste. The gas will be used to operate gas engines, the power from which will be employed for the generation of the required current for a small number of arc furnaces producing nitric acid from atmospheric nitrogen. The nitric acid produced will be neutralised by the ammonia from the by-product plant and the product will be ammonium nitrate. Thus the by-product plant will not only save the cost of the sulphuric acid now employed for the absorption of the ammonia, but will be making a valuable product instead.

The present production of nitric acid by the various arc processes is about 65,000 tons per year. If the suggestions made concerning the installation of small units at various power plants and at by-product plants are well received by those in charge of such enterprises we may expect to see within the next few years a great increase in production of nitrates by the arc processes.

Synthetic Ammonia Process.

A very recent method for the preparation of nitric acid has been referred to in the case of the cyanamide and the synthetic processes for making ammonia. In the operation of each of these processes some of the ammonia is oxidised to nitric acid, which is then combined with the balance of the ammonia resulting in the formation of ammonium nitrate. This method is a development of the Ostwald process for the oxidation of ammonia. In this process a mixture of ammonia and air in the proportion by volume of one of the former to ten of the latter is passed at a high speed through a platinum gauze heated to about 700° C. The gauze is made of wire 3/1000 of an inch in diameter and there are eighty meshes to the inch. The gas is passed at such a rate that the contact time is about 1/100 of a second. The platinum gauze is first heated by the passage of a current, but as the reaction is exothermic it is not necessary to maintain the heat during the oxidation.

If the ammonia and air mixture are passed through too rapidly the gauze is cooled below the reacting temperature and the ammonia passes through unchanged. If, on the other hand, the stream of gas is too slow, the oxidation may result in the entire loss of nitrogen by the formation of water and elementary nitrogen. The reaction aimed at is—



A great deal of work has been done to determine the best temperature, size of the catalyst, speed of the gases, and conditions of cooling to obtain the highest efficiency. This process is now so well controlled that an efficiency of well over 90 per cent is the usual practice.

What was said in regard to the necessity of rapidly cooling the nitric oxide obtained in the arc process applies here with equal effect, and the nitric oxide obtained by the oxidation of ammonia is cooled as rapidly as possible and further oxidised to nitrogen peroxide by the oxygen of the

air. The further details of making nitric acid by this process are the same as those already mentioned in the case of the arc process.

An interesting application of the process for the oxidation of ammonia to nitric oxide is employed in some modern sulphuric acid plants which produce sulphuric acid by the chamber process. Instead of employing sodium nitrate as the source of the oxides of nitrogen required for the catalyst in this process, a small installation of a modified Ostwald apparatus is installed and ammonia is oxidised as needed. This utilisation of ammonia is said to materially reduce the production cost of the sulphuric acid.

To summarise, the important compounds of nitrogen are ammonia and ammonium salts, nitric acid and the oxides of nitrogen, and the organic nitrogenous materials produced in agriculture. The sources of these compounds are Chilean sodium nitrate, bituminous coal, and atmospheric nitrogen. The processes of importance for the production of ammonia are the "natural" one of obtaining it as a by-product in the distillation of coal and other bituminous materials, the synthetic process for utilising atmospheric nitrogen, and the cyanamide process for making ammonia indirectly from the nitrogen of the air. The processes for making the oxides of nitrogen are the arc process for the fixation of atmospheric nitrogen and the oxidation of ammonia. Nitric acid is made by the interaction of nitrogen peroxide with water, the oxide of nitrogen being obtained by one of the processes just mentioned, and by the distillation of a mixture of sulphuric acid and sodium nitrate. Nitrogenous materials are produced in agriculture when nitrogenous fertilisers are employed in the cultivation of crops and in those cases where by symbiosis the atmospheric nitrogen is directly employed.

As to whether or not man by his efforts has prevented the nitrogen equilibrium from being upset in the wrong direction there is now no question. Even with a destructive war in progress enough nitrogenous material was being manufactured or rendered available to maintain the rate of loss for some time to come. Now that military demands have so nearly ceased, the supply of nitrogen compounds is far greater than the apparent immediate need. Have we gone too far in constructing plants for the production of nitrogen compounds? This is a question which only the future can answer. It is certainly a present fact that the production of nitrogen compounds is far greater than any peace demand which we could have imagined, and yet there are millions of acres of land which would richly respond to more intensive cultivation for which our stores of nitrogenous materials should be used. There must be a period of patient waiting and readjustment, and during this time we may be tempted to think that we have gone too far in the production of nitrogenous materials. But many thoughtful observers predict that finally there will be a demand for all our present production of nitrogen compounds, and more.

Man sought to maintain the nitrogen balance and to prevent loss in the supplies of a valuable material. Not only has he accomplished this but he has added greatly to the store. This feat, stimulated by the world war, may in time result in making conditions of living so sure upon the earth that we may forget the great destructions that would have been impossible but for nitrogen compounds, and remember rather the constructive effects of these same compounds in rebuilding the world.

Silvanus Thompson Memorial Lecture. — The Council of the Röntgen Society have pleasure in announcing that the second lecture, entitled "The Electrical Changes in Active Tissues," will be delivered by Prof. W. M. Bayliss, M.A., D.Sc., F.R.S., on Tuesday, May 9, 1919, at 8 p.m., in the Barnes Hall, at the Royal Society of Medicine, 1, Wimpole Street, London, W. 1.

NOTE ON THE EXTRACTION OF THALLIUM FROM PYRITES FLUE DUST.

By GEORGE SISSON and J. S. EDMONDSON.

DURING the progress of the war the Research Department of the Ministry of Munitions requested chemical manufacturers to investigate their waste products, with a view to recovering useful substances. They mentioned more particularly selenium from sulphuric acid works, this element being valuable on account of its property of altering its electrical conductivity when subjected to light of varying colour or intensity. In response to the above request, we collected for experiment a quantity of dust and refuse deposited in the flues of the sulphuric acid plant of the Blaydon Chemical Works. The flues mentioned lead the sulphur gases from the pyrites kilns into the Glover concentrating tower, and require to be cleared out periodically. The kilns are charged with copper pyrites from Spain. Such pyrites contain perhaps 2 per cent of copper and small quantities of a large number of other elements. Some of the constituents, such as arsenic, antimony, tellurium, thallium, selenium, are volatilised or burnt off with the sulphur, the iron, copper, &c., remaining in the burnt ore. The more volatile constituents, such as the sulphur, arsenic, and selenium, are carried forward principally beyond the flue into the Glover tower.

The flue dust itself consists of materials carried over mechanically such as iron oxide, small quantities of copper and lead, and volatile substances condensed at the flue temperature of about 450° C., such as antimony, bismuth, thallium, &c.

After making several experiments on this material we failed to separate any appreciable quantity of selenium; no doubt the temperature of that part of the plant was too high for condensation, the hot gases carrying forward into the sulphuric acid any traces of selenium contained in the pyrites.

We then turned our attention to thallium, which was known to occur in such deposits. In fact the metal was discovered in and isolated by Crookes from a similar deposit from the Harz Mountains ore (CHEMICAL NEWS, 1861, iii., 193, 303). Lamy also isolated a specimen from a lead-chamber deposit in 1862 (*Ann. de Chim.* [3], lxvii., 385).

Although thallium compounds are somewhat widely distributed they occur in very small quantities, associated with other metallic sulphides in various ores, and the flue dust of sulphuric acid factories is still the only practicable source. Such dust may contain up to 8 per cent, but only rarely is more than 0.25 per cent of thallium present. The quantity of dust we collected was about 15 cwt. in six months, representing the burning of 1500 tons of pyrites. The dust contained 0.25 per cent or a total of 4 lb. of thallium, equal to 1 part per million of pyrites.

The method we used to separate the thallium depends chiefly upon the sparing solubility of the chloride and the solubility of the sulphate, the operation being to treat the dust with boiling water acidified with sulphuric acid in a wooden or earthenware vessel, using live steam injection; on settling, the clear liquid is treated with hydrochloric acid. The crude chloride precipitate is separated, washed, and converted into sulphate by heating with strong sulphuric acid, the excess of acid is driven off, the remaining sulphate dissolved in water, filtered, and re-precipitated as chloride. The purified chloride after drying is mixed with potassium cyanide and sodium carbonate, and fused in a crucible, care being taken not to use too high a temperature in order to avoid loss by volatilisation. Or the chloride may be reduced by zinc and the resulting metal melted in a current of inert gas. Instead of hydrochloric acid sodium chloride may be used to precipitate the thallium from the sulphate solution. The crude dust must be washed repeatedly to extract the whole of the thallium salt. Several ounces of the metal were obtained by this method.

An alternative method is to precipitate the thallium as iodide from the sulphate solution, the iodide being less soluble than the chloride, but the cost of the iodide is an objection.

DISCUSSION.

Prof. P. PHILLIPS BEDSON suggested that it might be possible to take advantage of the change of colour which occurred on heating thallium iodide in determining the heat of bearings, as had been done in the case of mercuric iodide. He recalled that in 1901 he had assisted in a search for thallium among alkali waste materials, but without success.

Mr. EDMONDSON, in reply to a question, said that thallium was not found in all samples of pyrites.—*Journal of the Society of Chemical Industry*, xxxviii., No. 6.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 27, 1919.

Sir J. J. THOMSON, O.M., President, in the Chair.

THE following papers were read :—

"The Morphology and Evolution of the Ambulacrum in the Echinoidea." By H. L. HAWKINS.

A summarised account of the ambulacra in non-Holectypoid orders is given. *Bothriocidarid* shows the simplest type of structure, and the most efficient for coronal strength. As podia increased, ambulacral plates multiplied, and the areas became mechanically weak. The main podial function in Regular Echinoids being adhesive, coronal weakness demanded modification. In most Palaeozoic types, general flexibility neutralised local weakness; but with the adoption of rigidity the problem reappeared. Hence arose "plate-complexity."

The formation of compound plates is discussed. "Grouping" precedes, and is distinct from, combination. Plate-reduction is due to "growth-pressure"; combination to tubercle-growth. Elaboration of combination culminates in the Echinometridæ, where the compounds regain "Bothriocidaroid" proportions.

In Irregular Echinoids no combination occurs; grouping is often developed. Secondary specialisation in Spatangids produces "Palaeozoic" structures.

The Holectypoida show four ambulacral types :—

- (i.) Plesiechinid (triad-groups adorally, primaries adapically);
- (ii.) Pygasterid (primaries throughout);
- (iii.) Pyrinid (triad-groups throughout);
- (iv.) Discoidiid (triad-groups adorally, dyad-groups adapically).

Plesiechinid is primitive, and resembles the early Acrosaleniid type. Pygasterid indicates simplification, being morphogenetically transitional from Diademoid to Spatangid structure. Pyrinid is persistent, resembling the "Echinoid" structure of Diademoids. Discoidiid is exceedingly elaborate, showing extreme plate-reduction.

The Cassiduloidea are divided into Nucleolitoidea and Cassiduloidea (restr.). The former is related to the Pygasteridæ; its simpler members have Plesiechinid ambulacra, and Holectypoid structures appear in later forms. The Cassiduloidea evolved through the Echinonēidæ.

There are three main trends of evolution in Echinoid ambulacra :—(i.) Diademoid, attaining plate-combination; (ii.) Clypeastroid, attaining plate-destruction; and (iii.) Spatangoid, reversionary.

"The Genesis of Edema in Berib. i." By R. McCARRISON, M.D.

CHEMICAL SOCIETY.

Ordinary Meeting, March 6, 1919.

SIR WILLIAM J. POPE, K.B.E., F.R.S., President,
in the Chair.

THE PRESIDENT announced that Prof. Dr. T. Schlöesing, who was elected an Honorary and Foreign Member on June 16, 1892, died on February 8 last, and that Mr. Harry Shulman, who was elected a Fellow on February 18, 1915, had died on February 22.

Messrs. G. J. Woods, F. C. Savage, N. Makower, R. Bickmore, G. Higson, W. A. Nash, B. R. Heasman, C. Diamond, F. Peet, and W. C. Peck were formally admitted as Fellows of the Chemical Society.

The names of the Fellows recommended by the Council for election as Officers and as Ordinary Members of Council for 1919-1920 were read from the Chair.

Certificates were read for the first time in favour of William Herbert Fletcher Armstrong, B.A., Kbalsa College, Amritsa, India; Walter Hutton Crouch, 67, Wellington Road, Wanstead, Essex; James Ross Fraser, 13, Archibald Road, Tufnell Park, N. 7; James Edward Grainger, Lennards, Rainham, Essex; John Henry Harvey, Ravensworth, Llantarnam, Newport, Mon.; George Armand Robert Kon, B.A., 79, Cromwell Road, S.W. 7; Walter Shepherd, 103, Spital Road, Rochdale; Walter Bernard Smith, B.Sc., Marlborough College, Wilts; Ernest Henry Stenning, King William's College, Isle of Man; Frederick Thomas Stevenson, 48, Strathairn Street, Bermondsey, S.E.; Ralph William Ewart Stickings, B.Sc., Soudley House, Wandle Road, Morden, Mitcham; Stanley Goulden Thompson, 1, Thorn Bank, Manchester Road, Buxton, Derbyshire; Harold George Tribley, Yetminster, Sherborne, Dorset; Albert Edward Wallis, "Hillside," Sunbridge, Sevenoaks, Kent.

A certificate for election has been authorised by the Council for presentation to ballot under By-law I. (3) in favour of David M. Davies, H.M.S. *Cyclops*, care of G.P.O.

Prof. J. W. NICHOLSON, M.A., D.Sc., F.R.S., then delivered his lecture, entitled "Emission Spectra and Atomic Structure."

A vote of thanks to Prof. Nicholson for his lecture, proposed by Prof. W. H. BRAGG, F.R.S., and seconded by Sir JAMES DOBBIE, F.R.S., was carried with acclamation.

Ordinary Meeting, March 20, 1919.

SIR WILLIAM J. POPE, K.B.E., F.R.S., President,
in the Chair.

CERTIFICATES were read for the first time in favour of William Henry Barrett, Rossall School, Fleetwood; Robert Macfarlane Clark, B.Sc., 138, Bath Street, Glasgow; Harry Eade Dear, B.Sc., Littlecote, Widemouth Bay, Bude, Cornwall; Surindra Nath Dey, B.A., 38/1, Nilmony Mitter Street, Beadon Square, P.O., Calcutta, India; Reginald Gordon Doyle, 28, Newlands Park, Sydenham, S.E. 26; Frederick Freeth, 17, Victoria Road, Stockton Heath, Cheshire; Frederick John Spencer Hall, 4, York Road, Forest Gate, E. 7; Edward John Jones, 8, Windsor Street, Uplands, Swansea; Frederick George Mann, B.Sc., 21, Thurlby Road, W. Norwood, S.E. 27; George Stanley Withers Marlow, B.Sc., 37, Collington Road, Sydenham, S.E. 26; Frank Matthews, B.Sc., 12, Hurlingham Court Mansions, S.W. 6; James Morris, 23, Brynmor Crescent, Swansea; Marriappa Parthasarathy, 21, Maligakande, Colombo, Ceylon; John David McBeath Ross, M.A., B.Sc., 9, Ruskin Walk, Herne Hill, S.E. 24; Kalyan Chennakesava Srinivasan, M.A., Niton, 34, Pycroft's Road, Madras, S.E., S. India; Cyril Heath Stephenson, B.A., Darley Green, Knowle, Warwickshire; Ernest Turner, B.Sc., 28, Shrewsbury

Terrace, South Shields; Walter Wahl, Academy, Abo, Finland; Orr Walker, 29, Camden Street, Belfast.

The following papers were read:—

"The Rotatory Dispersive Power of Organic Compounds. Part IX. Simple Rotatory Dispersion in the Terpene Series." By T. M. LOWRY and H. H. ABRAM.

"The Formation and Stability of *spiro*-Compounds. Part II. Bridged-*spiro* compounds Derived from cyclohexane." By C. K. INGOLD and J. F. THORPE.

SOCIETY OF PUBLIC ANALYSTS AND
OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, April 2, 1919.

Dr. SAMUEL RIDEAL, President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Charles Frederick Lee Barber, A.I.C.; George Stanley Withers Marlow, B.Sc., F.I.C.; Frederick William Read.

Certificates were read for the second time in favour of Messrs. Madanlal Jekisandas Gajjar; James Sorley, F.I.C.

The following were elected members of the Society:—Messrs. Robert Odell Bishop, A.I.C.; Hubert William Bywaters, D.Sc., F.I.C., Ph.D.; Barnard Scott Evans, M.C., B.Sc. Lond., F.I.C.; Frank Scott Fowweather, M.Sc., A.I.C.; Robert Atkinson Oddy; William Branch Pollard; Charles Kenneth Tinkler, D.Sc., F.I.C.

The following papers were read:—

"A Method for the Determination of Monochlorobenzene in Mixtures containing Benzene, Monochlorobenzene, and Dichlorobenzene." By N. G. S. COPPIN, M.Sc., A.I.C., and F. HOLT, O.B.E., M.Sc., A.I.C.

The method is based upon Mr. D. Northall-Laurie's "Determination of Toluene in Commercial Toluols" (*Analyst*, 1915, xl., 384). 200 cc. of the dried sample are distilled at the rate of 7 cc. per minute; the first 50 cc. are collected, and after collecting a further 100 cc. exactly, the distillation is stopped. The first 50 cc. and the 50 cc. residue are each tested in special constant boiling-point flasks. From the boiling-points the percentages by weight of the constituents are read off from a graph.

The method gives direct results with an accuracy of 0.1 per cent for all mixtures containing from 50 to 100 per cent of monochlorobenzene.

"The Electrical Conductivity of Milk." By J. H. COSTE, F.I.C., and E. T. SHELBOURNE, F.I.C.

The examination of over 200 samples of milk shows that the conductivity is not sufficiently well defined to be useful as an analytical datum except for milks which have been examined by this means before incurring the risk of dilution. The relation between conductivity and temperature, non-fatty solids, ash, chlorine content, and free acid, and the effect of dilution, have been examined. It is pointed out that the results obtained are consistent with the explanation given by L. C. Jackson and A. C. H. Rothera that the conductivity is dependent on the extent to which the constant osmotic pressure of milk is due to electrolysis with which the milk-sugar is complementary.

"Note on Soluble Lead in the Glaze of Casseroles." By HELEN MASTERS, B.Sc.

Casseroles of various descriptions, particularly some said to be of French make, were found to yield considerable proportions of lead on treatment with 4 per cent acetic acid, and with dilute solutions of other acids such as would be present in certain cooking operations. The soluble lead is not all extracted by one operation, but after two or three treatments each subsequent treatment appears to yield a fairly constant quantity.

SOCIETY OF GLASS TECHNOLOGY.

THE March meeting of the above Society was held in the University (Mason College), Birmingham, on Wednesday, March 18.

After the usual formal business, the following paper was read :—

"The Preparation of Raw Materials for, and the Casting of, Glass Pots." By B. J. ALLEN.

The author dealt first of all with the deflocculation of clays, and showed how it could be accomplished by electrical treatment. He described a simple apparatus for testing clays to show their suitability under this electrical treatment. His experiments have proved that many common fire-clays altogether unsuited in their ordinary state for the manufacture of refractories could by the above treatment be made to produce a large proportion of highly satisfactory material fit to meet the specification for high grade work.

Mr. Allen dealt briefly with the manufacture of pots by the old method of building by hand, and dwelt briefly on the limitations of this method. It is most difficult for the pot maker to guarantee a perfectly united homogeneous pot. It is very essential that clay and the grog be in intimate contact in the finished pot, and this is ensured by the casting of the pot. He then went on to describe in detail the preparation of slip and subsequent casting of pots. He also described in detail different types of pots. The lecture was well illustrated by lantern slides and specimens, and the lecturer gave it as his opinion that research on all these matters should be carried out by the Society.

During the morning, members, at the kind invitation of the Directors in each case, had the opportunity of visiting Messrs. Icknield Glass Works (Oslers), Ltd., Freeth Street, Birmingham, and Messrs. P. Branscomb, Glass (Bottle) Works, Adderley Street, Birmingham.

The members are reminded that the annual general meeting will take place at the University on April 16.

OBITUARY.

SIR JAMES MACKENZIE DAVIDSON.

WE regret to have to announce the death of Sir James Mackenzie Davidson, M.B., C.M., which took place at his residence, 26, Park Crescent, Portland Place, on April 2nd.

Sir James was for many years Consulting Surgeon to the Röntgen Ray Department of the Charing Cross Hospital. He took a very prominent part in the early development of the medical application of X-rays, and was among the first to recognise their value in Surgery, becoming one of the most enthusiastic workers in the science. His method of localisation laid the foundation of all subsequent development in this most important branch of X-ray work, and his apparatus is indispensable in practical radiography.

Sir James's researches upon X-rays, radium, and allied phenomena are very extensive; among the more important are—Stereoscopic Radiography and Fluoroscopy, Precise Methods of Localisation of Foreign Bodies in the Eye, contributions to the Physics of the X-Ray, and a Mercury Interrupter for Induction Coils.

His laboratory was always full of interesting work, and he spared no pains or expense in developing his many inventions, working with his own hands.

His well-merited Knighthood was conferred upon him in recognition of his work in the application of X-rays to Medical Science. His striking personality and genial manner will cause him to be greatly missed in his large circle of collaborators.

NOTES.

AT the meeting held at the College of Technology, Manchester, on January 17, 1919, a paper was read by Mr. Joseph Barnes, on "The Properties and Uses of Some Titanium Compounds," chiefly with regard to its interest to dyers and colorists. The value of titanium compounds in the dyeing industry was recognised by the author forty years ago, who found that this element as well as zirconium gave colour reactions very like alumina. At that time titanium was looked upon as one of the rare elements, but its abundance and wide distribution has since been recognised, and it has been classed by F. W. Clarke as twice as plentiful as carbon. Large quantities of titanium salts are used by leather dressers. The more important salts used are titanium sodium sulphate, titanium potassium oxalate, titanium-tanno-oxalate. The specimens dyed by the aid of titanium that were exhibited by the author were greatly admired.

INVESTIGATIONS carried out by W. E. Tottingham at the Wisconsin Agricultural Experiment Station, Madison, U.S.A., show that during the change in a fermenting mixture of cow and horse manure an increase in nitrogen was apparent after three and four weeks, the increase being much greater in straw-littered than in unlittered manure. The results showed that the manure contained nitrogen-fixing bacteria of considerable activity, especially when mixed with straw. The chief agent in nitrogen fixation is said to be *Bacterium azophile*, n. sp.

ONE thing that the war has brought very much into prominence is the preparation of "substitutes." Germany in particular has specialised in this direction. A substitute for milk appears to have been the following:—250 grms. of ground sweet almonds to a litre of water. From the physical, chemical, and alimentary point of view, it approaches very nearly cow's milk. No difference can be perceived when used with tea or coffee. The most suitable after sweet almonds are Brazilian nuts. The following fruits can also be employed, but are not so suitable:—Soya beans, earth nuts, walnuts, cocoanuts, hazel-nuts, and acajou nuts.

PROF. ANDREW GREY's new treatise on Gyrostatics and Rotational Motion is an extremely interesting and valuable publication that we hope to review later. The gyroscope has played an important part in military and naval devices during the war and is likely to be applied to many purposes in the future. The very full practical and theoretical treatment of the subject by Prof. Grey, whose work is well known, is likely to be of great use.

M. CESARI (Vétérinaire-major) has made some experiments upon the substitution of albumen from horse blood for white of egg in cooking. Omelettes, rice cake, waffles, &c., in which serum replaced white of egg, were pronounced very good. It was pointed out that 10 litres of serum, at a cost of about 1s. 6d., would replace the whites of 200 eggs worth at least 24s.

THE spring meeting of the American Chemical Society will be held in Buffalo early in April. A full and interesting programme has been arranged, in which both social and official functions appear to be well proportioned. The secretary makes a strong appeal for the enrolment of new members, suggesting that "a chemist who is not a member of the American Chemical Society must feel lonesome."

THE struggle between M. Pasteur and the medical profession in the early days of his career is well known, and "The Life of Pasteur," by René Vallery-Radot, and other works, give full accounts of that wonderful fight. But it is interesting to read that the story has been dramatised at the Vaudeville Theatre, Paris, in a five act play, and is said to have had a very favourable reception, which is all the more remarkable owing to the curious nature of the piece without a plot or a female character, the "human interest" being the struggle and victory of the scientist.

THE estimated consumption of soda-ash in Canada is now 50,000 tons. During the past four years the lack of soda-ash has been felt by a great many of our industries. They were entirely dependent on foreign supplies. Most of the soda-ash used in Canada came from England, and, with the war, Canada was practically shut off from supplies. Now, however, the Brunner, Mond, Canada, Limited, have their new plant at Amherstburg, Ont., practically completed, and they are in a position to supply Canadian requirements. They are using the "Solvay Process," by which practically all the soda-ash now produced is made. The town of Amherstburg is well situated, and the raw products—salt, limestone, and ammonia—are easily available. A tract of land of 650 acres was secured, and a main building, 170 by 190 feet and ten stories high, was erected. The plant has one of the largest lime kilns known, being 80 feet high. Taken altogether, it is one of the most complete soda-ash plants in the world, and is designed in such a way that the capacity may be readily increased with the demand. The company produces its own power, and obtains its salt from wells practically at the plant. The limestone used is also taken from quarries on the property. The produced soda-ash is of general use in the manufacture of glass, soap, paper, wood-pulp, paints, leather, enamelled ware, cleansers, textiles, oil refining, metal working, and metallurgical operations, washing powders, chemicals, and drugs.

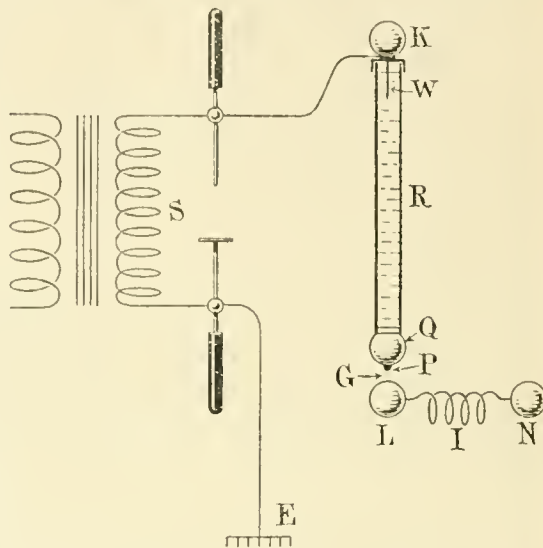
THE March issue of *The Industrial League Journal* includes a twelve page supplement of an address by The Rt. Hon. G. N. Barnes, M.P., to managers and foremen on "Industrial Matters." Mr. H. Blain, of the London Underground Railways, contributes a very interesting article on "Industrial Honour." There are special contributions from Mr. Woodman Burbidge, Sir Eric Geddes, R. Young, M.P., The Rt. Hon. G. H. Roberts, M.P. (Food Controller), Prof. Kirkaldy, W. C. Bridgman, M.P. (Parliamentary Secretary Board of Trade), Sir William Bull, M.P., G. J. Wardle, M.P. (Parliamentary Secretary, Ministry of Labour), and Tom Shaw, M.P. An article on "League of Nations" and "Industrial Unity" is contributed by Major The Hon. Waldorf Astor, M.P. There is also a full account of the splendid donation of £20,000 by Colonel Sir William Dupree towards creating industrial harmony. Altogether the Journal maintains its very interesting character.

THE DECIMAL ASSOCIATION, 212 and 213, Finsbury Pavement House, are issuing quarterly an interesting little booklet, "The Decimal Educator." In a circular letter they state:—"There is a general consensus of opinion that the reform in British coinage and weights and measures for which we are working should be taken in hand during the period of reconstruction. To enable us so to educate public opinion that this object should be attained, we require the help and co-operation of all who are in favour of our aims, and I hope, therefore, that you will see your way to becoming a member of the Decimal Association. Pamphlets giving the arguments which we put forward in support of our demand for reform will be gladly sent to anyone applying for them."

THE EASTERN KODAK COMPANY have undertaken the preparation of a very complete series of pure chemicals, chiefly those used in photography. The list is very full and the supply will be of great use to those occupied in photographic research. They will probably be available in this country.

Mr. G. G. BLAKE, Assoc.I.E.E., in the *Archives of Radiology and Electrotherapy* describes a simple method of obtaining static electricity from an induction coil. A diagram of the apparatus used is here given. R is a glass tube containing a solution of alcohol and water; it is fitted with two terminal electrodes, Q and P, the latter being connected to one of the secondary terminals of an induction coil S, its other electrode Q terminates in a blunt

point P. The prime conductor of the machine consists of two metal spheres, L and N (about 2 in. diameter), connected to one another by means of a fine wire inductance or choke I; by raising or lowering the resistance tube R, the distance between point P and sphere L can be varied. The inductance is introduced here to damp out any high-frequency oscillations that may be set up. It is well known that such oscillations are always produced when a



spark passes between two electrodes, they are in fact the origin of Hertzian waves. That this choke has a beneficial effect was actually tested by experiment. It is important to connect the other terminal of the secondary of the induction coil to earth, as shown at E. This has the effect of increasing the intensity of the discharges, and at the same time it helps to prevent the production of inverse current, consequently purer discharges are obtained. In the initial stages of the experiments the secondary terminal of the coil was earthed through a condenser and not directly.

NOTES FROM FOREIGN SOURCES.

Thermic Decomposition of certain Inorganic Trinitrides.—E. Moles.—In 1916 Tiede (*Ber.*, xlix., 1742) published an account of a study of the thermic decomposition of metallic trinitrides in vacuo. He gave the initial temperature of decomposition and that of the regular liberation of nitrogen for the azides of K, Na, Rb, Cs, Ba, Sr, and Ca, and stated that the decomposition is quantitative for all these compounds, the N_2 set free is very pure, and that the metal is deposited in the form of a mirror in the case of the alkaline metals, and as a blackish powder in the case of the metals of the alkaline earths. These results suggested to the author the idea of applying the thermic decomposition of the azides in the revision of the atomic weights of these metals. Values would thus be obtained which were quite independent of that of the atomic weight of Ag, and the value for N would be established with an accuracy exceeding $\pm 1/14000$. He found that the initial temperature of decomposition of AgN_3 is about 300° and that then the gas is evolved very regularly at 280° . But later experiments showed that the decomposition is not as perfect as had been imagined, the weight of the metal obtained by difference being always too great. The value obtained

for sodium were 23.024, 23.086, 23.10. The author is studying the decomposition of NaN_3 and KN_3 and intends to continue these researches on the revision of atomic weights of the metal of the alkalis and alkaline earths.—*Journal de Chimie Physique*, 1918, xvi., 401.

Oxidation of Nitric Oxide by Dry Air.—André Sanfourche.—The reaction between nitric oxide and dry air takes place in two stages, with very different velocities; the first, which is extremely short, corresponds to the formation of nitrous anhydride N_2O_3 , while the second and longer stage leads to the formation of peroxide N_2O_4 . At the ordinary temperature the velocity of both reactions has been shown by the author and M. P. Jolibois (*Comptes Rendus*, 1919, clxviii., 235) to be not appreciably influenced by the proportion of air. The author has now studied the influence of temperatures lying between -50° and 525° upon the same velocity. The results show that the temperature does not appear to have any effect upon the very great velocity of the reaction $2\text{NO} + \text{O}_2 = 2\text{N}_2\text{O}_3$, which is complete in a fraction of a second, but on the other hand it profoundly modifies the course of the reaction $2\text{N}_2\text{O}_3 + \text{O}_2 = 2\text{N}_2\text{O}_4$ (or 4NO_2). This reaction, which is also very rapid below 0° , is complete up to about 200° , but occurs more and more slowly, this difference being possibly connected with the dissociation of N_2O_4 . Above 200° there is a tendency to establish the equilibrium $2\text{N}_2\text{O}_3 + \text{O}_2 \rightleftharpoons 4\text{NO}_2$. The displacement of the equilibrium takes place from right to left as the temperature is raised from 200 to 600° .—*Comptes Rendus*, 1919, clxviii., 307.

Precipitated Amorphous Silica.—P. Braesco.—Precipitated and calcined silica has usually been known under the name "amorphous silica." The only reason for regarding it as amorphous is that no crystals of definite form can be distinguished, either with the naked eye or under the microscope. But it is well known that similar precipitates, like so-called amorphous barium sulphate, are really crystallised, and the author has investigated the true nature of "amorphous" silica by determining some of its physical properties. Measurements of its dilatation were performed, using Chévenard's apparatus and starting either with silica obtained by the decomposition of sodium silicate with hydrochloric acid, or else with silica obtained by the decomposition of silicon fluoride with water. In both cases the results obtained were the same. When silica is precipitated, dehydrated, and heated only to 600° it behaves exactly like vitreous silica, and has the same low coefficient of dilatation. It is thus true amorphous silica. But when it is precipitated and calcined at a temperature above 1000° there is an abrupt change of dilatation between 220° and 240° , and silica calcined above 1000° is not amorphous silica, but crystallised silica of the cristobalite variety.—*Comptes Rendus*, 1919, clxviii., 343.

Action of Alkalis on Crucibles made of Alloys of Platinum and Gold.—Paul Nicolardot and Claude Chatelot.—These experiments were performed in order to find out whether new platinum is less attacked than old platinum when alkalis are fused with it, and whether the presence of iridium increases or decreases its resistance to the same alkalis. The fusions were all carried out similarly, 5 grms. of alkali being used, and the process occupied ten minutes, the source of heat being a spirit lamp. The crucibles were first weighed, then the fusion was carried out, and they were then washed with water and dried. They were found to have lost weight, and their clean shining surface had been blackened. This black deposit disappears on treatment with hydrochloric acid. The loss of weight of metal is considerable, and is always greater when potash is used than with soda. New crucibles are more resistant than old ones, and the presence of iridium does not increase the resistance, but rather the reverse. The presence of copper does not seem to be as deleterious as that of iridium.—*Bulletin de la Société Chimique de France*, 1919, xxv.-xxvi., 4.

Determination of Zirconium.—Paul Nicolardot and Antoine Reglade.—The formation of a phosphate in an acid medium has been used by Hillebrand to analyse zircons, and it seemed to be of interest to find out whether the precipitation of zirconium is really complete in presence of iron, chromium, and aluminium. The reaction would be characteristic of zirconium, since bismuth, which is very rarely associated with it, is the only element which could be determined in these conditions. The authors have carried out a series of tests to determine the effect of the acidity of the solutions of foreign salts and of the time of contact with the reagents before filtration. The salt used was pure nitrate of zirconium, and the foreign salts added were those of iron, aluminium, and chromium. The results showed that ammonium phosphate in an acid medium (20 per cent at least of sulphuric acid) is a characteristic reagent for zirconium in presence of iron, aluminium, and chromium, and bismuth is the only other element which is precipitated in these conditions.—*Comptes Rendus*, 1919, clxviii., 348.

Cycle of Oxidation of Nitrogen Dioxide in Presence of Water.—André Sanfourche.—The reaction which is generally supposed to take place between nitrogen peroxide and water can be represented by the equation $3\text{N}_2\text{O}_4 + 2\text{H}_2\text{O} = 4\text{HNO}_3 + 2\text{NO}$. The study of the velocity of oxidation of nitrogen dioxide, however, suggests that nitrous anhydride may play some part in the reaction, and this hypothesis can be verified by bringing into intimate contact vapour of nitrogen peroxide mixed with an excess of air and water or more or less diluted nitric acid. The experiments show that in the oxidation of nitrogen dioxide in presence of water nitrous anhydride is the intermediate product and not nitrogen peroxide. Nitrous anhydride is oxidised by nitric acid of sufficient concentration with formation of nitrogen peroxide and water; this reaction is limited by the inverse reaction. Thus there must be equilibrium for a certain concentration of nitric acid, and experiments show that this concentration is in the neighbourhood of 50 per cent.—*Comptes Rendus*, 1919, clxviii., 401.

Substitutes for Platinum in Electrolytic Apparatus.—Paul Nicolardot and Jean Boudet.—Metals or alloys which are to be used to replace platinum in electrolytic apparatus must be unalterable even in moist warm air containing sulphuretted hydrogen. They must be able to be washed with water and dried without change of weight, and must resist the action of pure nitric acid. They must remain unaltered during electrolysis in the liquids generally employed—sulphuric and dilute nitric acids, dilute ammonia, aqueous solutions of sodium sulphide and cyanide. They must also possess the mechanical qualities necessary to enable them to be worked up into the usual shapes of electrodes. Various commercial alloys have been investigated by the authors for the purpose, and they have found that the most suitable is an alloy of gold containing—gold, 920 parts; silver, 50 parts; copper, 30 parts. It is very resistant towards nitric acid. In the case of the anode the surface must be covered with a very thin layer of platinum (0.005 grm. per square cm.) by electrolysis, to protect it against oxidation. The alloy can be used as such for the cathode.—*Bulletin de la Société Chimique de France*, 1918, xxiii.-xxiv., 387.

MISCELLANEOUS.

Atoms, Electrons, and Valency.—With the more recent views of the disintegration of matter, chiefly the result of the discovery of radium, the electro-positive and negative character of the elements come into play. The constancy of mass and weight are involved in their disintegration, and a dual variable electric character might

be ascribed to the elements. With regard to mass the measure of which is weight, the force of gravity, there is still needed an efficient theory of this force, and, admitting the disintegration of matter, such factors as atomic heat and gas volumes are more the essential properties of the atoms. If the atomic weights are considered in relation to the periodic law, most attention has been given to the relationship existing in the several groups. The increase of atomic weight in the horizontal period, may have some relation to valency, and in the latter half of the periodic table the halogens which, classed as heptads, are monovalent with the alkali metals in the first half, valency being a more complex function of the constitution of the elements. Taking the increase of atomic weight as affecting valency, in the periods and the group relationship as to weight, atomic volumes introduce the conception of space. The views of the disintegration of matter may be advanced not only by considering the radium elements but ionisation in liquids and the electric discharge in rarefied gases. — J. C. THOMLINSON.

Geological Society.—At the Annual Meeting, held February 21, the following Medals and Awards were presented:—

Sir AUBREY STRAHAN, K.B.E.—The Wollaston Medal.
Miss GERTRUDE L. ELLES, Sc.D.—The Murchison Medal.

WILLIAM FRASER HUME, D.Sc.—The Lyell Medal.

Major Sir DOUGLAS MAWSON, D.Sc.—The Bigsby Medal.

ALEXANDER LOGIE DU TOIT, D.Sc.—Balance of the Proceeds of the Wollaston Donation Fund.

Mrs. ELEANOR M. REID, B.Sc.—Balance of the Proceeds of the Murchison Geological Fund.

Mr. JOHN PRINGLE.—Moiety of the Balance of the Proceeds of the Lyell Geological Fund.

STANLEY SMITH, D.Sc.—Other moiety of the Balance of the Proceeds of the Lyell Geological Fund.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 7th inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. The decease of Sir James Mackenzie Davidson, a Member and a Manager of the Royal Institution, was announced, and a Resolution of Condolence with Lady Mackenzie Davidson and her Family was passed. Miss A. Campbell, Dr. C. B. D. Campbell, Mrs. E. H. Campbell, Mr. J. D. Campbell, Mr. R. G. Campbell, Mrs. E. Davies, Miss H. M. Douglas, Mr. G. K. B. Elphinstone, Mr. J. W. Evans, Mr. C. W. Hawksley, Captain A. J. Hollick, Lord Leigh, Miss I. H. Mond, and Mr. R. A. Yule were elected Members.

Oxygen a Revolutioniser of Industry.—(From the *Technical Supplement*, Feb. 18).—Due to the rapid growth of the nitrate industry based on the fixation of atmospheric nitrogen, the cost of oxygen has fallen enormously since the outbreak of the war. This great achievement in science, whereby oxygen is made a by-product of an important manufacture, is likely to work a revolution in industry. The uses of oxygen, when cheaply produced, are almost endless. Gas manufacturers will not be slow to utilise it to increase the light of their burners where a strong illumination is required; for that purpose new forms of burners will be called for. In metallurgical operations a small percentage of oxygen blown into the furnaces will raise the temperature considerably. In such cases it will allow inferior and cheaper qualities of coal to be used. Carbide of calcium will be produced in the blast-furnace by a purely thermic method. Alumina will be reduced by carbon. Auriferous quartz will be melted. The glass industry will be revolutionised by the easy fusing of all forms of quartz. A new chemistry, viz., that of the electric furnace, will be created. The manufacture of sulphuric acid will be much accelerated by the powerful oxidation of sulphurous acid. The production of ozone, or electrified oxygen, opens up numerous vistas, notably

for the sterilisation of drinking water and the maintenance of a wholesome atmosphere in factories, workshops, schools, theatres, barracks, hospitals, underground railways, and mines. For use in mines it may be of inestimable service.—*Bulletin de la Société de l'Industrie Minérale*, Third Issue, 1918.

MEETINGS FOR THE WEEK.

MONDAY, 14th.—Ceramic Society, 7. (In the Central Schools of Science and Technology, Stoke-on Trent). "Substitution of Apatite for Bone-ash in the Bone China Body," by N. B. Davies. "Heat Conductivity of Porous Materials and the Heat Insulation of Kilns," by J. W. Mellor. "Casting of Heavy Pottery," by B. J. Allen.

TUESDAY, 15th.—Institution of Petroleum Technologists, 5.30. "Some War Problems of Petroleum Supply," by Sir Frederick W. Black.

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THE CHEMICAL NEWS

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SOME AMERICAN DOLOMITES.

By BURLEIGH B. REED.

THESE rocks are among the important building stones of the country and have a wide distribution. We secured a few typical specimens from different sections in order to make a comparison of their chemical composition. The specimens analysed are all used as building materials in their respective localities.

1. From Mount Vernon, Iowa, and belongs to the Niagara formation, the oldest member of the Silurian age. It is hard and compact, and has a yellowish tint due to the presence of iron. Analysis as follows:—

	Per cent.
SiO ₂	1.29
Fe ₂ O ₃ and Al ₂ O ₃	0.57
CaCO ₃	55.17
MgCO ₃	43.04
Total	100.07

2. Dolomite from Westchester County, New York, not far from New York City. It is a white crystalline rock, and is a coarsely granular marble in appearance. The formation belongs to the Cambro-Silurian, and is thought to be equivalent to the Stockbridge limestones of the Housatonic Valley in Massachusetts. It is quite a typical dolomite in composition, not materially different from the Iowa rock. The analysis as follows:—

	Per cent.
SiO ₂	2.71
Fe ₂ O ₃ and Al ₂ O ₃	1.05
CaCO ₃	53.43
MgCO ₃	42.93
Total	100.12

3. From Lockport, New York, also belonging to the Niagara formation. There was upon the dark grey rock an incrustation of milk-white crystals. The analysis of the body of the rock, which was hard and compact, resulted as follows:—

	Per cent.
SiO ₂	2.76
Fe ₂ O ₃ and Al ₂ O ₃	1.42
CaCO ₃	51.85
MgCO ₃	43.94
Total	99.97

The specimen contains a sufficiently high percentage of magnesium to class the rock as a fairly typical dolomite.

4. The white crystals encrusting the specimen:—

	Per cent.
SiO ₂	0.18
Fe ₂ O ₃ and Al ₂ O ₃	1.21
CaCO ₃	81.62
MgCO ₃	17.15
Total	100.16

This varies quite widely from a true dolomite as the calcium has largely replaced the magnesium. The

amount of silica is unusually small, as might possibly be expected from the crystalline structure of the material.

5. From Bertram, Iowa. This belongs to the Niagara formation which lies between Mount Vernon and Cedar Rapids. The rock is grey in colour with numerous small light coloured crystals disseminated through the mass. Some analytical data had been found which seemed to indicate that the magnesium content of the rock was in excess of the calcium. Our analysis was made with a view to determine whether this was really the case. Two concordant results obtained are as follows:—

	Per cent.
SiO ₂	0.90
Fe ₂ O ₃ and Al ₂ O ₃	0.90
CaCO ₃	55.61
MgCO ₃	42.58
Total	99.99

The figures indicate a rather typical dolomite, as one would naturally expect from the analysis of similar specimens in the neighbourhood.

The analyses were made by the methods outlined in the revised edition of Knight's "Quantitative Analysis."

Cornell College, Mount Vernon, Iowa,
March 17, 1919.

PHYSICAL CHEMISTRY AND ITS BEARING ON THE CHEMICAL AND ALLIED INDUSTRIES.*

By Prof. JAMES C. PHILIP, O.B.E., M.A., Ph.D., D.Sc.

(Concluded from p. 173).

THE validity of the foregoing equation being thus established it may be employed to calculate for even temperatures and a number of pressures the maximum quantities of ammonia obtainable by the interaction of nitrogen and hydrogen. These figures, constituting a summary of the influence of temperature and pressure on the ammonia equilibrium, are presented in the following table [valid for 1 vol. nitrogen + 3 vols. hydrogen]:—

Temp. cent.	Equilibrium percentage of ammonia at—			
	1 atmo.	30 atmo.	100 atmo.	200 atmo.
200°	15.3	67.6	80.6	85.8
300°	2.2	31.8	52.1	62.8
400°	0.44	10.7	25.1	36.3
500°	0.129	3.62	10.4	17.6
600°	0.049	1.43	4.47	8.25
700°	0.022	0.66	2.14	4.11
800°	0.002	0.35	1.15	2.24
900°	0.00069	0.21	0.68	1.34
1000°	0.0044	0.13	0.44	0.87

From the physico-chemical standpoint then the conditions which affect the position of the ammonia equilibrium are thoroughly understood, and their influence can be definitely formulated. Plainly, the highest percentage conversion of nitrogen and hydrogen into ammonia is to be secured by working at a high pressure and a low temperature. There is, however, a limit to the pressure under which a large scale process can be carried out conveniently and safely, and the pressure employed in practice is not above 150–200 atmospheres. The use of high pressures such as those just quoted leads not only to a favourable displacement of the equilibrium, but also to an increased rate of approach to the equilibrium position.

* Cantor Lecture (I.). Delivered before the Royal Society of Arts, December 2, 1918. From the *Proceedings of the Royal Society of Arts*, XVII., No. 3450.

A limit is set also to the reduction of temperature, which from the point of view of yield alone is desirable, by the difficulty of finding catalysts which are sufficiently active below 500–600° C. From the point of view of technical production the rate at which the reaction takes place is naturally of prime importance, and this comes back really to the question of the activity of the catalyst employed.

Of itself the reaction $N_2 + 3H_2 = 2NH_3$ takes place very slowly at temperatures below 1000°, and it is only in the presence of catalysts, such as osmium, uranium, and iron, that the formation of ammonia becomes reasonably rapid at temperatures where the yield is still moderately satisfactory. In the manufacturing process a mixture of nitrogen and hydrogen at a pressure of 150–200 atmospheres is passed over the catalyst at a temperature of 500–600° C., the small quantity of ammonia formed is removed by refrigeration or absorption, and the residual gases are again circulated over the catalyst. High yield and rapid establishment of equilibrium are not reconcilable, and a balance has to be struck at the temperature which gives the best economic results.

In working out the most satisfactory conditions for the technical synthesis another factor has to be considered, and that is the rate of circulation of the gases over the catalyst. If this rate is high the percentage of ammonia formed per passage will fall a good deal short of the equilibrium percentage, but, on the other hand, there will be all the more passages in a given time. It has, indeed, been shown by Maxted that for a catalyst chamber of given size the highest yield of ammonia per hour is obtained with a very high rate of circulation and a minimum value for the percentage of ammonia formed per passage. This is made clear by the following record, obtained with an iron-potash catalyst at 550° C. and 150 atmospheres:—

Time of contact of gas with catalyst in seconds.	Per cent ammonia formed.	Yield of ammonia in kilos per hour per litre of catalyst space.
0.34	0.65	2.7
0.56	0.94	2.3
1.8	1.8	1.4
3.6	3.2	1.25
7.2	4.7	0.91

From recent information, for which the writer is indebted to Mr. Maxted, it appears that with a somewhat more active iron catalyst and extremely rapid circulation, yields of ammonia up to 10 kilos per hour per litre of catalyst space may be obtained. There are, however, difficulties in the construction of satisfactory heat exchangers for the commercial utilisation of such rapid circulation. The optimum rate of circulation must be determined for each plant.

The fact that in actual working, where a moderately high rate of circulation is employed, the percentage of ammonia does not reach the equilibrium value, involves the possibility that a rise of temperature may even lead to an increase in the yield of ammonia per passage. This has been found to occur in some experiments carried out by Maxted at 530° and 580° C.

Catalyst—iron potash. Time of contact in seconds.	Pressure—150 atmos. Percentage of ammonia formed at—	
	530°.	580°.
0.6	0.96	1.5
1.0	1.3	2.4
1.5	1.7	3.2
2.0	2.05	3.8

Such an increase in the yield accompanying a rise of temperature can occur only when the yield is much less than the maximum obtainable—i.e., the equilibrium value. At a higher range of temperature, where the establishment of equilibrium is very rapid, a rise of temperature will lead to a decrease, not an increase, of the ammonia yield.

It has been shown above that the displacement of the ammonia equilibrium with rise of temperature is represented by the equation—

$$\log_{10} K = \frac{2098}{T} - 2.5088$$

$$\log_{10} T - 0.0001006 T + 0.186 \times 10^{-6} T^2 + 2.1,$$

and the values of K given by this formula are in good agreement with the figures obtained experimentally up to 1000° C. If the validity of the formula is assumed for still higher temperatures it follows, as shown by Maxted, that the decrease of K with rising temperature continues up to a point about 2500° abs., but that a further rise of temperature should be accompanied by an increase of K. The approximate position of K appears from the following calculated figures:—

T° abs.	K × 10 ⁴ .
1500	0.63
2000	0.26
2500	0.21
3000	0.28
3500	0.55

It should be noted that where the displacement of equilibrium with rising temperature is reversed, the heat effect of the reaction must pass through a zero value. This follows from the thermodynamic equation—

$$\frac{d(\log_e K)}{dT} = - \frac{Q}{RT^2}.$$

The prediction of an increased yield of ammonia at extremely high temperatures, a prediction based, it must be admitted, on a very extensive extrapolation of the formula for K, has been verified by Maxted's experiments. In these a mixture of nitrogen and hydrogen was introduced into an oxy-hydrogen flame, and then cooled with extreme rapidity to the ordinary temperature. The gas was then found to contain appreciable quantities of ammonia, estimated in one case to be equivalent to 1.23 per cent by volume at an absolute pressure of one atmosphere. Rapid cooling is essential, otherwise the equilibrium shifts to the unfavourable position characteristic of the temperatures between 1500° and 3000° abs. The passage of a nitrogen + hydrogen mixture through a capillary tube in which a small high-tension arc is burning leads also to the formation of appreciable quantities of ammonia. It will be interesting to see whether this thermal synthesis of the gas can be effected on anything else than the very small scale which has so far proved practicable.

The catalytic synthesis of ammonia at moderate temperatures, on the other hand, has come rapidly to the front, and has played no small part in the war technology of Germany, where the process was being developed on the large scale in the period 1912–14. During the war synthetic ammonia was turned out in that country at a rapidly increasing rate, and it is stated that the quantity of ammonium sulphate produced by this method has recently amounted to about half a million tons per annum. The significance of this synthetic ammonia industry lies in the fact that the product can be readily oxidised to nitric acid, which, of course is the indispensable basis of explosives. The fixation of atmospheric nitrogen, however, will be required to meet the needs of peace also, in respect of nitrogenous fertilisers, and in all probability the catalytic synthesis of ammonia has a future before it independent of the demands of war.

In final illustration of the value of the principles of chemical equilibrium in the rational survey and control of a technical gas reaction, one or two points connected with the water gas reaction $CO_2 + H_2 \rightleftharpoons CO + H_2O$ may be discussed. There are an equal number of molecules on the two sides of this equation, and it therefore follows that

a shift of the equilibrium involves no change of volume. Hence in conformity with Le Chatelier's principle already referred to, an alteration of the pressure is without effect on the position of equilibrium.

The equilibrium constant in this case is defined as $K = \frac{c_{CO} \cdot c_{H_2O}}{c_{CO_2} \cdot c_{H_2}}$, where c_{CO} , c_{H_2O} , c_{CO_2} , and c_{H_2} are the

equilibrium concentrations of the different gases concerned. The reaction being reversible it is possible to approach the equilibrium from either side, and in the actual investigation of the reaction the value of K was deduced from two sets of experiments—(a) those in which mixtures of carbon dioxide and hydrogen were passed through a heated quartz or porcelain tube containing platinum as a catalyst; (b) those in which mixtures of carbon monoxide and water-vapour were treated similarly. An analysis of the gas mixture issuing from the tubes gave the values of the equilibrium concentrations. As an example of the results obtained under (a) the following, recorded at 986° C., may be quoted:—

Percentage Composition of the Initial Mixture.

CO ₂ .	H ₂ .
10.1	89.9
30.1	69.9
49.1	51.9
60.9	39.1
70.3	29.7

Experiments carried out at the same temperature with initial mixtures of carbon monoxide and water-vapour gave a mean value of 1.55. The agreement of this number with the average of the figures for K recorded in the table shows that the equilibrium between the four gases, whatever their initial concentrations, is established in conformity with the mass action law.

As regards the shift in the equilibrium with rise of temperature the direction of the shift can be deduced from the known heat effect of the reaction $CO_2 + H_2 = CO + H_2O$. At the ordinary temperature the occurrence of this reaction from left to right is accompanied by the absorption of about 10,000 calories, and hence a rise of temperature will favour the system $CO + H_2O$ at the expense of the system $CO_2 + H_2$. Quantitatively this is shown by the increasing values for K obtained with rising temperature. Thus the figures for the constant at 686°, 786°, 886°, 986°, and 1086° are 0.53, 0.84, 1.20, 1.57, and 1.96 respectively.

The water gas equilibrium is of interest in relation to the manufacture of hydrogen, the demand for which has steadily increased during the last five or ten years. Apart from its use in connection with airships and balloons, there are various newer industries, in which the gas is required on a large scale, as, for example, in the hardening of fats and in the synthetic ammonia industry. Among other methods for the manufacture of hydrogen in quantity it has been found possible to make the hydrogen of water available by first producing water gas, and subsequently passing the water gas with excess of steam over a catalyst, such as alkaline ferric oxide, at a temperature of 500–600°. The raising of the concentration of the water-vapour must plainly shift the equilibrium in the reversible reaction $CO_2 + H_2 \rightleftharpoons CO + H_2O$ over towards the left, and in actual practice it is found that the carbon monoxide of the water gas is almost completely converted into carbon dioxide by this treatment, and that there is a corresponding increase in the quantity of hydrogen. Thus, in one case on record, a water gas containing 24 per cent carbon monoxide was found, after one passage over the catalyst at 500° with excess of steam, to contain only 2 per cent of this gas. Naturally the carbon dioxide and the residual carbon monoxide must be removed by condensation or absorption if pure hydrogen is required.

Percentage Composition of the Equilibrium Mixture.

CO ₂ .	CO+H ₂ O.	H ₂ .	K.
0.70	9.46	80.38	1.59
7.18	23.00	46.82	1.58
21.36	27.88	22.88	1.59
34.20	26.61	12.58	1.64
47.66	22.79	6.76	1.61

MECHANICAL PHILOSOPHY AND THE SECOND LAW OF THERMODYNAMICS.

By FRED. G. EDWARDS.

THE atom of the ether is a tetrahedron of mass one-fourth of the hydrogen molecule ($3.2 \times 10^{-24} = 0.8 \times 10^{-24}$ gm., and assuming the specific density of the ether determined below at 0.575 its atomic volume will be 1.39×10^{-24} cc. equal to a sphere of diameter 1.39×10^{-8} cm. Its atomic domain is defined by an ascribed rhombic dodecahedron, but as each atom collides with four only of the twelve contiguous atoms the whole formation is divided into two interpenetrating plena. The specific density D of the ether may deduced as a first approximation at 0.575 from the formula $R = R_1(D/D_1)^{1/2}$, where R_1 is the refractive index ($= 2.4669$), and D_1 the density ($= 3.5$) of diamond, and $R = 1$. The pressure of the ether is now directly deduced at 5175×10^{17} dynes per sq. cm. from the radiation velocity by the formula $c = (p/d)^{1/2}$, where $c = 3 \times 10^{10}$ and $d = 0.575$.

It has, perhaps, been too readily assumed that an atomic ether besides a density and a pressure must also have a temperature; but the real physical interpretation of the second law of thermodynamics for solids and liquids will now be deduced in terms of atomic motion. To the above formula may be added a ratio-factor, thus $a = (p/k/d)^{1/2}$, where $k = 1$ in the case of light travelling through a frictionless ether. But in the case of sound in ethyl-ether-vapour the ratio of the specific heats $k = c_p/c_v = 1.06$, and the reciprocal ratio h of the intramolecular energy over the rectilinear molecular energy deduced from the thermodynamic formula $h = (5 - 3k)/(3k - 3)$ is 10. This means that if there be one quantity-intensity unit of atomic energy, radiating or absorbing heat evidenced as temperature, there are ten other quantity units of energy in the form of intramolecular motion. The energy of this non-radiating motion is pure entropy. But when $k = 1$ then $h = \infty$, or the whole of the energy is entropy, and there is no temperature, as the intensity factor $= 0$. This is the limiting condition for solids and liquids, but is inapplicable to gases where the free energy is molecular and the size of the molecule is not infinite as in the former cases.

The hydrodynamic pressure of the ether on a circular area of diameter 5.3×10^{-11} cm. would be 41.8 dynes, and if two spherical cavities at one diameter apart centre to centre mutually repel with this force their repulsion at 1 cm., inversely as the distance squared, would be 1.17×10^{-19} dynes as against 1.16×10^{-19} dynes in the case of electrons. Only by such a structure would a massless electron remain in a material universe. The diameter is less than 10^{-2} times that of the calculated ethereal volume, so that its formation by the removal of a "positive" atom involves four tetrahedrally inclined strains in the ether, corresponding to the lines of force, which on a conductor would be reduced to one free line or tube of force. The electron theory is true, but it is a developed negative from which a positive picture should be formed.

The mathematical theory of electro-dynamics is a special form of the theory of elasticity. The electrical work done by a planet moving through an apparently stagnant ether reappears as energy in gravity. The centripetal radiations of gravity are the cause of apparent

irrelativity, and also the source of the sun's energy now admitted to be 10^8 times greater than can be otherwise accounted for. The quantum is a function of atomic mass, and should be the momentum of an atom as it strikes the ether in striking an electron, and Planck's constant would be the unit action of the ether in the formation of waves.

Radiation is thus energy in the form of momentum travelling through a material fluid as visualised by Maxwell, but he was not bold enough to deduce the density and pressure of the medium by the ordinary laws of mechanics, doubtless because at that time he considered the first law of dynamics applicable to produce temperature. Stokes, Kelvin, and Helmholtz have shown that direct action at a distance, now exclusively used in electrical theory, is mathematically identical with the action of an incompressible fluid. That fluid, which formed the foundation of his great electrical theory and which he repeatedly insisted upon, is now specified with its electronic displacement.

March 29, 1919.

ARSENIOUS OXIDE AS A STANDARD SUBSTANCE IN IODIMETRY.

By ROBERT M. CHAPIN.

Introduction.

FOLLOWING the development of a reliable laboratory method (*Journ. Ind. Eng. Chem.*, 1918, x., 522) for the preparation of pure arsenious oxide, an investigation has been made of the accuracy possible when the substance is employed in iodimetry. Though the process has long been in common use it seems never to have received the rigorous testing demanded by modern standards. The work of Washburn (*Journ. Am. Chem. Soc.*, 1908, xxx., 31) extended merely to a study of the precision possible, that is, the closeness of agreement among titrations. The work here presented involves the direct comparison by titration with weight burettes, of known amounts of pure arsenious oxide and pure iodine. The object was to establish the reliability of properly purified arsenious oxide as a standard to replace the less convenient iodine which has been the final recourse in work calling for the highest possible degree of accuracy. This substance is the simple oxide of an element of very accurately determined atomic weight; it is non-hygroscopic, permanent in the solid state, and also highly permanent in a properly acidified solution.

Preparation of Pure Substances.

Arsenious oxide was obtained in the form of a coarse powder nearly free from dust by resubliming some material purified in the manner already referred to. (The raw material comprised several grades; chiefly "technical" white arsenic).

Pure iodine was obtained by a process abridged from that of Guichard (*Ann. de Chim.*, 1917, vii., 27). Potassium iodide U.S.P., 100 parts, and iodine U.S.P., 150 parts, were dissolved in water, 100 parts. To the solution was added about 5 parts crystallised copper sulphate in warm concentrated solution. After thorough stirring and standing for some time the precipitate was filtered off and the filtrate distilled from a retort into a cooled flask, water being added as necessary. The iodine in the distillate was filtered with suction on a hardened paper in a Buchner funnel, washed with water, and redistilled with water from the same apparatus. After again filtering, washing and draining, it was thoroughly dried over calcium chloride, then sublimed twice with intermediate drying. The subliming apparatus consisted of a shallow beaker, on the rim of which rested a globular flask filled with cold water. During the second sublimation the substance was not collected until a liberal preliminary portion had been

allowed to escape, and it was obtained in loose crystals by frequent removal from the condensing flask. It was finally ground to coarse powder in a glass mortar, and preserved over calcium chloride.

Preparation of Solutions.

The solution of arsenious oxide in dilute sulphuric acid, as recommended by Roark and McDonnell (*Journ. Ind. Eng. Chem.*, 1916, viii., 327) appears for obvious reasons the safest method of preparation. The only question is the possible volatilisation of an appreciable quantity during the necessary boiling, and therefore the following experiment was conducted.

Experiment 1.—In a side-tube distilling flask was placed 5 cc. concentrated H_2SO_4 in 300 cc. H_2O . Flask and condenser were fitted with bark corks. The distillate, collected in portions of 25 cc. and tested for arsenic in a modified Gutzeit apparatus, yielded a very low blank. To the remaining 200 cc. liquid in the flask was then added $2\frac{1}{2}$ grms. As_2O_3 , and distillation was resumed, successive portions of 25 cc. being taken off while the volume in the flask was maintained at 100 to 200 cc. All portions collected except the first, which contained less, owing to delayed solution of the substance, showed a constant content of 20 microgrms. As_2O_3 . Finally the condenser tube was filled with 50 cc. diluted H_2SO_4 and left one-half hour. No more As_2O_3 was found in this solution than in the blank.

Therefore, in the preparation of one litre of tenth-normal arsenious oxide solution it would be necessary to boil off more than 600 cc. in order to diminish the strength of the finished solution by 1 part in 10,000. (Since hardly a fourth of the above proportion of liquid need be lost through gentle boiling in a long-necked volumetric flask, any such additional precaution as a reflux condenser, which has been suggested as an absolute preventive against loss, is obviously superfluous).

About 0.8 gm. dry arsenious oxide was weighed out by difference from a vial into a weighed 100 cc. volumetric flask. To avoid loss of dust the vial was chosen small enough to slip easily within the neck of the flask during transference of the substance. Solution was effected by very gentle boiling in a mixture of 16 cc. of dilute sulphuric acid (1 in 10) with about 60 cc. water. Water was then added to the cooled solution up to the base of the neck of the flask and a second weighing was made.

For weighing the iodine, ampules were prepared by blowing a bulb of slightly less than 2 cm. diameter on the end of a glass tube of 5 mm. bore, which was further drawn down to about 2 mm. at 1 to 2 cm. above the bulb, and lastly cut off to a total length of about 11 cm. Into the bulb of this miniature flask was charged through a slender tube 1.5 cc. of a solution of C.P. potassium iodide (10 grms. per 15 cc.) without wetting the interior of the apparatus above the constriction. After the weight, constant on the balance for ten minutes, had been ascertained, about 0.8 gm. iodine was introduced, most of which remained above the constriction. The tube was drawn out above the iodine to a capillary, which, after cooling to room temperature over calcium chloride, was sealed off by a small blow-pipe flame. The tip thus separated was gently heated to remove condensed iodine, and finally, after cooling, the weight of tube plus tip, constant for ten minutes, was ascertained, and consequently the weight of iodine obtained. A tube treated in a similar way, except that no iodine was added, showed a variation in weights before and after sealing decidedly less than 0.1 mgrm.

All weights, including burette readings, were reduced to vacuum and the weights of the two substances themselves were further corrected by means of the Bureau of Standards certified corrections for the set of weights employed.

The water used was freshly collected from a large laboratory still of a modern type which delivers water substantially free from dissolved gases. All solutions were employed shortly after preparation.

Execution of the Titrations.

In the ordinary titration of arsenious oxide with iodine, sodium bicarbonate is the buffer usually employed to maintain neutrality and is entirely appropriate for the purpose. For the reverse titration here contemplated it presented obvious defects. The sodium phosphate mixture advocated by Washburn appears to react with inconvenient slowness. A borax-boric acid mixture was also stated by Washburn to be theoretically applicable but was not regarded by him as practically so useful as phosphate or bicarbonate. Barneby (*Journ. Am. Chem. Soc.*, 1916, xxxviii, 330) found such a mixture useful in "differential iodimetry." It effects a rapid reaction and is otherwise entirely convenient. The proportion of boric acid necessary to prevent the formation of iodate was determined by the following experiment:—

Experiment 2.—To 50 cc. of a solution containing recrystallised $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, with or without H_3BO_3 , was added 50 cc. N/20 I. After standing twenty-two hours an excess of H_3BO_3 was added and the solution was titrated with $\text{Na}_2\text{S}_2\text{O}_3$ (N/100 at end) and starch. Then diluted HCl was added in excess and the liberated iodine titrated with N/100 $\text{Na}_2\text{S}_2\text{O}_3$.

TABLE I.—Formation of Iodate in Presence of Borax and Boric Acid.

No.	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ Grms.	H_3BO_3 Grms.	N/100 $\text{Na}_2\text{S}_2\text{O}_3$ Cc.
1.	0	0	0.00
2.	5	0	9.15
3.	5	1	1.90
4.	5	2	0.10

It appears, therefore, that a buffer solution containing borax and boric acid in the weight ratio of 2 to 1 may be used with entire safety as respects formation of iodate. The solution adopted contained 8 per cent of crystallised borax and 4 per cent boric acid.

With this fact established the following experiment was carried out to test the accuracy of the method:—

Experiment 3.—A tube of iodine, thoroughly shaken to dissolve all the substance, was placed in a stout 500 cc. bottle of clear glass, to which was also added 30 cc. of a freshly prepared 10 per cent solution of pure potassium iodide and 125 cc. of the buffer solution. After cooling the whole to about 10°C ., the tube of iodine was shattered by pressure with a stout glass rod and an arsenious oxide solution was run in from a weight burette to decoloration. After adding 2 cc. of freshly prepared starch solution the final end point was reached by cautious titration with N/100 iodine (see Note 1). For the blank (see Note 2) another bottle was charged with 40 cc. potassium iodide solution, 125 cc. buffer solution, 2 cc. starch and water to equalise volumes, and the mixture cautiously titrated with the N/100 iodine solution until the colours in the two bottles matched. The volume of N/100 iodine needed for titration of excess arsenious oxide was in no case more than 2 cc. and for the blank never more than 0.2 cc. The colours were not significantly affected by further addition of the buffer mixture, nor by longer standing. The results calculated from the titrations appear in Table II., under Tests No. 1 to 4.

After this work had been completed there appeared a paper by McCrosky (*Journ. Am. Chem. Soc.*, 1918, xl, 1662) in which it was stated that perfectly dry iodine was obtained only by fusion in the weighing tube, a procedure which affected his results by more than 1 part in 700. In contrast with McCrosky the present writer had not passed a continuous current of cold water through his subliming apparatus and had noted no condensation of moisture thereon, while in the final sublimation the substance was collected only after considerable heating, possibly only after complete fusion. But the uncertainty necessitated further work. The following experiment was therefore carried out:—

Experiment 4.—In a 2 cc. glass-stoppered weighing tube about 0.8 gm. iodine was fused as described by McCrosky and, after weighing, the tube with loosened stopper was dropped into a 500 cc. funnel-necked glass-stoppered Erlenmeyer flask containing 7 cc. of 40 per cent potassium iodide solution. Into the funnel around the stopper was poured 3 cc. of the potassium iodide solution, and after all iodine had been dissolved, this, followed by 125 cc. of borax buffer, was allowed to flow down the sides of the flask. The titrations were made as previously described and the results are given in Table II. under Tests 6 and 7. Test 5 was made without fusion on a sample of the original iodine which had been contained in a glass-stoppered weighing bottle resting in a dark cabinet during seven months.

TABLE II.—Comparison of Iodine and Arsenious Oxide.

No.	As_2O_3 sol.	Weight I. Weight As_2O_3 .
1.	A	2.5664 (a)
2.	A	2.5657
3.	B	2.5661
4.	B	2.5658
5.	C	2.5656
6.	C	2.5661
7.	D	2.5659
Average ratio determined . .		2.5658
Theoretical ratio by 1918 official atomic weights . .		2.5651
Difference		0.0007

(a) Excluded in computing average.

Evidently the original iodine was perfectly dry, and pure iodine is not hygroscopic. Evidently, too, the cumbersome method of weighing employed in the first four tests offers no advantage over the use of a stoppered weighing bottle with proper precautions. Fusion before weighing, though unnecessary in the present case, is certainly a desirable precaution. Excluding the unsubstantiated result of Test 1, the greatest variation of any test (No. 3 and No. 6) from the average was therefore 1 part in 8500, while the average of the observed ratios differed from the theoretical ratio by less than 1 part in 3600. The difference is in the direction which indicates a less purity, or a greater loss during manipulation of the iodine, and consequently is in favour of arsenious oxide as the more reliable standard in practice.

Precautions in the Preparation and Use of Standard Iodine Solutions.

Aside from correct standardisations, iodine solutions intended for accurate work demand some special precautions previously known in a general way but rarely observed. The first of these is the use of potassium iodide in quantity sufficient not merely to dissolve the iodine in concentrated solution but to inhibit dissociation of potassium tri-iodide, and consequent ready volatilisation of iodine after dilution to standard strength. The proportion of double the weight of iodine in twentieth-normal solutions authoritatively recommended is unquestionably too low (*Journ. Assoc. Official Agr. Chemists*, 1916, ii.; "Report of Comm. on Edit. Meth. of Anal.," p. 63), for loss of strength during a series of titrations with such a solution as ordinarily manipulated may be readily demonstrated. Since potassium iodide is a high-priced substance each worker must decide for himself what proportion the character of his work warrants him in using. The writer has adopted the proportion of 4 per cent in both tenth-normal and twentieth-normal solutions in which a high degree of accuracy and permanence is desired.

The presence of iodate in an iodine solution may naturally cause variation in its apparent strength according to whether titrations are conducted in a neutral or acid

medium. Though commercial potassium iodide appears generally to be free from iodate there are some grounds for the suspicion that iodate may be formed in iodine solutions under certain conditions of storage (Deiss, *Chem.-Ztg.*, 1918, xxxviii., 413). It may be tested for by the procedure described under Expt. 2, and if present may be removed by addition of the corresponding amount of sulphuric acid.

A final precaution is to attain the end-point with starch at a temperature not above 25° C. It is well enough known that the blue colour of iodised starch disappears completely on slight heating, but in fact warming even to 30° C. is sufficient to affect distinctly the delicacy of the end-point.

Summary.

It was found that by employing weight burettes with appropriate precautions, six titrations of pure arsenious oxide against pure iodine gave highly precise results, the average of which agreed within 1 part in 3600 with the theoretical value. The evidence is in favour of arsenious oxide as the more reliable standard substance in practice. Precautions in the preparation and use of standard iodine solutions are emphasised.—*Journal of the American Chemical Society*, xli., No. 3.

Notes.

1. The starch solution contained 0.5 per cent potato starch, boiled two hours with water, plus 3 per cent boric acid added towards the end of the boiling period. A briefly boiled starch solution is revealed under a magnifying glass as a suspension of enormously swollen granules. When such a solution is used as an indicator the resulting colour is located partly in the granules and partly in the medium; not an ideal condition if delicacy of end point is a paramount consideration. Though still visible after a half-hour, granules can no longer be detected after one hour of boiling, while boiling for an additional hour appears to effect no further change. Long boiled solutions are equally as sensitive as solutions boiled only two minutes. The tints afforded with minimal amounts of I are likewise entirely comparable, ranging from pure blue through violet to rose as the concentration of KI and other salts is increased. Boric acid, not previously used as a preservative for starch solutions so far as the writer is aware, appears to be very effective against moulds, though not against salivary enzymes. Solutions used intermittently during several months, and closed only by a pipette or inverted beaker, appear indistinguishable from fresh solutions. In contrast solutions of soluble starch prepared by acid hydrolysis soon suffer degradation.

2. The truth of the blank obtained by this procedure has been questioned. In the first place, making the justifiable assumption that NaI produced from 0.8 gm. I will exert exactly the same effect upon the end-point as an equivalent amount of KI, particularly in the presence of a preponderating amount of the latter salt, it will be noted that the equivalent of 4.04 grms. KI was present in the regular run against 4.0 grms. in the blank. Secondly, the volumes of buffer and starch solutions were the same, while the colours were matched at equal final volumes. From previous experience assurance was felt that, provided equal concentrations of KI and approximately equivalent concentrations of total salts were maintained in order to equalise the salt effect upon the end-point, no specific effect would be produced by the minor differences in composition which existed. On the contrary it was feared that far greater risks of error would be incurred through the introduction of extraneous substances in an attempt to make the composition of the solutions exactly similar. But the possible magnitude of error in the blank has now been investigated. To a "true" blank should be added 1H derived from 0.8 gm. I, As₂O₃ derived from 0.312 gm. As₂O₃ and 6.24 cc. of the H₂SO₄ solution. There remained in hand the identical solution of H₂SO₄ originally

used, and this was diluted and boiled. A stock solution of As₂O₃ was made from the originally used As₂O₃ by oxidation with HNO₃ (Menzies and McCarthy, *Journ. Am. Chem. Soc.*, 1915, xxxvii., 2021). Since HI could only be introduced in the form of KI, a corresponding reduction of 1.2 grms. borax and an increase of 0.78 grms. H₃BO₃ is called for in the buffer. The various buffer solutions necessary were made from single bottles of the chemicals. Various mixtures of the above ingredients were titrated with N/200 I and starch in a total volume of 200 cc. to the first appearance of a plain and persistent colour, whatever the tint might be. The titrations were made by allowing the I solution to drop constantly from a burette at the rate of a drop in three seconds, the drops actually entering the titration being caught at half-minute intervals. Frequent tests showed that 1 cc. was very consistently delivered in 32 drops. The following table gives the results obtained:—

Run No.	KI Grms.	H ₃ BO ₃ Grms.	Na ₂ B ₄ O ₇ ·10H ₂ O Grms.	H ₂ SO ₄ sol. Grms.	Oxidised As ₂ O ₃ Grm.	N/200 I Drop.
1.	1	0	0	0	0	2—3
2.	4	0	0	0	0	3
3.	4	5	0	0	0	2—3
4.	4	5	10	0	0	5—6
5.	4	5	8	0	0	5—6
6.	4	6	8	0	0	5
7.	4	6	8	7	0	4
8.	4	6	8	7	0.4	4—5

It will be noted that, although the mixtures were made up slightly to exaggerate possible effects, the original blank, represented by Run 4, falls behind the true blank, Run 8, by at most 2 drops N/200 I. Next, to a mixture prepared as in Run 8 was added 13 drops (0.406 cc.) of N/200 I, and a mixture prepared as in Run 4 was titrated by the drop method at half-minute intervals until the colours matched. Triplicate comparisons showed between 16 and 17 drops to be necessary, and no difference between the final tints could be detected. Therefore the original blank falls behind the true blank by at most 4 drops N/200 I, or 0.125 cc. This quantity represents 0.00008 gm. I or a maximum error of 1 part in 10,000, which may possibly have occurred in the blank as originally obtained.

GREEK EXHIBITION.

As stated in the attached speech, the Exhibition in Athens of British Manufactures had its origin in a suggestion made last October by the important delegation of Greek business men who toured industrial England under the auspices of the Federation of British Industries. Having investigated, through a Special Commissioner, the extraordinary scarcity of every kind of manufactured article in Greece and the neighbouring Balkan and Levantine countries, the Federation agreed with Greek opinion that an Exhibition would offer very extensive opportunities to British manufacturers. The Exhibition, therefore, is now in active process of organisation.

The Greek Government, as part of its support of the idea, has lent for the purpose of the Exhibition the "Zappeion" building, close to the Royal Palace and the centre of the town, and specially and admirably constructed for Exhibition purposes. Although applications for space have been received only during the last three weeks or thereabouts, already a third or more of the available space has been taken up. Nearly all the most important branches of British manufacture are already represented.

In addition to the "Zappeion," the Greek Government has granted the use of an extensive piece of land on which

an "Extension" is being erected. This will house such of the larger exhibits as cannot conveniently be placed in the "Zappeion," and it will afford an admirable practical exposition of such articles as agricultural machinery, since land and space are available on which they can be shown actually at work.

As is well-known, the policy of M. Venizelos, and of the strong majority he represents, is to develop both the existing agriculture of Greece and the manufacturing industries she does not yet, but ought to, possess. In view of this, of course, the Machinery Section of the Exhibition will be of very great importance. The Exhibition will, however, appeal to a very much larger field than Greece alone. The trade of Asia Minor, Turkey, and, to a great extent, the Balkan countries, is almost entirely in the hands of Greece. Special arrangements are being made to interest these distant traders and to bring them to the Exhibition. Thence they will carry back with them their impressions of British products, and, most important of all, they will have had an opportunity of coming into contact with the representatives of firms in the Exhibition, and of forming a firm foundation for future business.

Major Kennard, the Federation's Commissioner to Greece, who is shortly to be established permanently in Athens, has been touring all the principal industrial centres of England giving manufacturers the benefit of his experience. The interest he has excited has been very great. In many cases manufacturers have been astonished by the information he was able to give them regarding present trade conditions and opportunities in the Near East—opportunities to which other nations are already very keenly alive, as is shown by the efforts they are at present making to establish themselves in the Levantine market. The accompanying notes are a condensed version of the address Major Kennard has been giving.

EXTRACTS FROM LECTURE BY MAJOR E. KENNARD.

You will probably all of you remember the visit of the Greek Commercial Delegates to this country last autumn, and I think it was the interest aroused by that visit that first gave birth to the idea of having a commercial representative of the Federation in Greece. It was also the members of the Greek Mission who suggested an exhibition of British industries to be held in the "Zappeion" Building in Athens.

The day after my arrival in Athens I visited the "Zappeion," and although, from the descriptions given to me by the members of the Greek Mission, I was prepared for something rather special in the way of buildings, I must confess that the actual sight of it almost took my breath away. It stands in the very best part of the town, at the top of a gentle slope, within a few minutes walk of all the leading hotels, and close to the tramlines. From the steps you see the Acropolis, close to you, on your right; on the left is the Stadium, seating 40,000 people, and constructed entirely of white marble (of which most of you have no doubt seen illustrations), whilst, in the foreground, is a large open gravel space, and beyond that again gardens full of palm trees, orange trees, &c., with a delightful glimpse of the sea in the far distance.

His Majesty's Minister, Lord Granville, from the moment of my arrival, took the deepest interest in the plans of the Federation, both as regards the Exhibition and the extension of British trade in Greece and the Near East generally, and throughout my stay rendered me every assistance in his power.

During the two months I was in Greece, I talked with people of all classes, chiefly commercial, both English and Greek, and never did I hear any other opinion except that the idea of holding an Exhibition of British Industries in Athens as soon as possible after the conclusion of Peace was the very best possible means of forwarding the interests of British commerce in the Near East. I say "Near East" advisedly, for though, at the moment, we are concentrating on Greece, and there is no doubt an immense

volume of remunerative trade to be done there, you should remember that Greece only forms a small portion of the Balkans and Levant.

With regard to noting the outlets for British produce in Greece, I would particularly urge upon your attention that owing to the fact that Peace has not been actually signed, Greece is at the moment the only country in that part of the world which is readily approachable from a commercial standpoint, but you should look upon Greece merely as a stepping-stone (an important one, I admit) to the trade of the whole of the Balkans and Levant. Fifty or sixty years ago Great Britain had practically a monopoly of that trade, but, from various causes, this was gradually wrested from us and secured by Germany and Austria; not only secured, but very largely increased. Before the outbreak of war it looked as though this trade was lost to us for ever, but owing to the events of the last four years Germany and Austria have been temporarily (I say advisedly "temporarily") knocked out, and we have now an opportunity which I think you will agree with me, we are unlikely ever to have again. The Greek nation is at present extremely Anglophile, and you must remember that there is a very large Greek element spread throughout the Balkans and Levant which, once we have secured our proper share of the trade of Greece herself, should be of the utmost assistance to us in obtaining a similar share of the trade of those other countries. At this moment it might almost be said to be ours for the asking. I don't think I exaggerate when I say that the Greeks would rather buy British goods than any other. They would rather trade with us than with any other nation, but they are at the moment absolutely denuded of every kind of commodity, from boot-laces to locomotives, and they must be supplied immediately, from some source. I can give you a small incident which will bring home to you the absolute lack of the most ordinary necessities of life at present prevailing in Greece. During my stay there I had a rather severe attack of influenza, and the medicine that was supplied to me by the leading chemist of Athens arrived in a ginger-beer bottle, stopped with a piece of newspaper. That other nations are bidding strongly for the trade of the Near East is proved by many facts, amongst others I may tell you that the American Consul-General for Greece applied for three Vice-Consuls during my stay in Athens. At the moment I maintain that we hold a distinct advantage over other competition. I am sure I am right in saying that if Greece at this moment were in a position to select one nation from amongst the nations of the world, to whom she would give the whole of her trade, that nation would undoubtedly be Great Britain, but you must remember that Greece is not in that position. Anglophile though she may be she has to live. Naturally she will try to obtain the best goods in the cheapest market. Not only will she try to obtain them, but in the unfortunate position in which she now is, she must obtain them *at once*. Greece believes, and I firmly believe that she is right in this belief, that the best of everything, from fighting men to metal-ware, is to be found in Great Britain. She has this belief at the moment, but it will not last for ever. Other nations are leaving no stone unturned to prove to her that they can fill her needs as well as we can. Not only that, but some of them advance the tempting argument that they are in a better position to give to her immediate delivery than we are. I therefore venture again to suggest to you the advisability of taking the long view, and of supplying immediately those commodities of which she is in such dire need.

I have had the honour—my use of the word "honour" is no *façon de parler*—of meeting M. Venizelos and many of his Ministers, and I am in a position to state that it is the intention of the Greek Government to develop Greece in all directions, Political, Agricultural, Mineral, and so forth. I know for a fact that the present Government has already taken steps in this direction, and I know something of their plans for the future.

This war has seen the connection by rail of the ports

Piræus and Salonica for military purposes, and I have reason to believe that this railway is to be developed for commercial purposes. Think what this means—a trunk line throughout the length of the land, with a statesman at the head of affairs who is passionately devoted to, and a firm believer in, the future welfare of this country. Greece is full of undeveloped mineral wealth, and from this trunk line will radiate branch lines, giving, in themselves, opportunities to British manufacturers. Further than that, you are aware that in any country, developed or undeveloped, the arrival of a railway means an increase in the population and industries of the regions through which that line passes, and this means yet more outlets for British produce—outlets which in the near future you will be so anxiously looking for in vain if you do not seize present opportunities.

At the commencement of my remarks I told you that one of the first objects for which I was sent out to Greece was to inspect, and if I thought fit, to secure the use of, the "Zappeion" Building for our Exhibition of British Industries. I took the precaution of sending commercial men, both English and Greek, on the spot, as to the advisability of holding the Exhibition, for I foresaw that if the Exhibition was organised, advertised, and proved a failure, it would lead to great disappointments both in Greece and at home.

I would point out to you that the Exhibition which we propose to hold will be in its way unique. Big Exhibitions of various kinds have been an almost common annual event in all parts of the world in pre-war days, but I think I am right in saying that this Exhibition of British Industries will be extremely practical. It will be a purely selling Exhibition. I venture to assert that every exhibitor who can guarantee immediate, or at all events quick delivery of bulk to the samples which he exhibits, will not only pay his expenses but will make a very large and immediate profit, without undue expense or risk. Further than that, he will have the comfortable feeling that he is doing his bit for his country in the great economic war upon which we are now embarked.

We will hold this Exhibition on such a scale that it will attract all classes of buyers, not only from Greece but from many or all of the Balkan States and the Levant. As I said before, all these countries need everything, and need it at once.

The Greeks have plenty of money, and—born traders that they are—they are longing to turn it over, and they want British goods. Are you going to supply them? I should like to see British products in every shop and every home in the Near East. It is up to you manufacturers to bring about this very desirable state of affairs. To show you that the Greeks themselves have a similar feeling, I may tell you that I brought with me from Greece an offer from a Greek gentleman to put up the sum of £40,000 towards the erection of a depot for purely British goods in Athens, on the understanding that it would be organised and run by Englishmen.

Remember that in arranging this Exhibition the Federation has no axe of its own to grind; its one and only object is to promote the interests of its members, and, through them, the interests of British Industries as a whole.

I have taken up a most unconscionable amount of your valuable time, for which I humbly apologise. The excuse I offer is that I have been on the spot, I have studied the conditions, and although I frankly confess that I started as a pessimist, I equally frankly confess that I have returned to this country a real optimist as to the possibilities for British trade in the Near East, using Greece and our Exhibition as a stepping stone.

Institution of Electrical Engineers.—At the meeting on April 24, at the Institution of Civil Engineers, Great George Street, Westminster, at 6 p.m., Major A. C. Fuller, R.E., will read a paper on "The Fullerphone and its application to Military and Civil Telegraphy."

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, April 3, 1919.

Sir J. J. THOMSON, O.M., President, in the Chair.

THE following papers were read:—

"Note on the Intensity Decrement in the Balmer Series." By T. R. MERTON, D.Sc., and Prof. J. W. NICHOLSON, F.R.S.

Twelve members of the Balmer series of hydrogen have been observed in vacuum tubes containing a trace of hydrogen in helium at a pressure of 41 mm. of mercury. In contrast with the diffuse appearance of the last of these members in pure hydrogen, they were observed in the present instance as sharp though faint lines.

A quantitative comparison of the intensity distribution in these tubes containing pure hydrogen, water-vapour, and a mixture of hydrogen and helium at low pressure, has shown that the visibility of the higher members of the series in the high pressure tubes is most probably due to the fact that the energy under these conditions is concentrated within narrow limits of wave-length, instead of being distributed through a broadened line whose energy content is, in fact, greater.

The observed results seem to be incompatible with the quantum theory of the hydrogen spectrum developed by Bohr.

"Determination of the Secular Accelerations of the Moon's Longitude from Modern Observations." By Prof. E. W. BROWN, F.R.S.

"Inter-crystalline Fracture of Metals under Prolonged Application of Stress." By W. ROSENHAIN, D.Sc., F.R.S., and S. L. ARCHBUTT.

The authors' observations have shown that in a number of metals, including lead, mild steel, and an alloy of aluminium with zinc and copper, the prolonged application of stress will, in certain cases, produce an abnormal type of fracture in which the crystals become separated from one another, instead of being broken or torn across in the normal manner. An exact similarity to this type of fracture is found in the "season cracking" of brass. In the latter case the applied stress is an internal one arising from elastic deformation. The authors base an explanation of this type of fracture on the hypothesis, formerly advanced by one of them and widely accepted among metallurgists, that the constituent crystals of metals are held together by thin layers of an amorphous inter-crystalline "cement," whose properties resemble those of a greatly under-cooled liquid. When stresses are applied to such an aggregate, the viscous under-cooled liquid films behave, in the first instance, like a very strong and hard material (somewhat resembling glass), and when fracture is brought about at any ordinary rate it occurs by the failure of the crystals themselves and not by the tearing away of one crystal from another. Under the prolonged action of stress, however, the viscous cement will, in favourable circumstances, yield slowly, so that the crystals become detached from one another. Whether this will occur or not must depend upon the character of the inter-crystalline boundaries; if these are rough and irregular, viscous flow will be prevented, but if they are very smooth it will be facilitated. The authors' observations show that in the cases where inter-crystalline failure occurs the metal has been subjected to some annealing process which has allowed the crystals to acquire smooth regular boundaries; where such smooth boundaries do not exist this type of failure is not met with. The practical importance of avoiding such "over-annealing" is pointed out. As the viscosity of a liquid rapidly decreases with rising temperature, it would follow that inter-crystalline failure of this

type will be favoured by a slight rise of temperature; this is known to be the case with brass, and the authors point out that cases of inter-crystalline cracking in steel have mainly been met with in the plates of steam boilers working at high temperatures.

"Zonal Harmonics of High Order in Terms of Bessel Functions." By J. R. ARREY, D.Sc.

A formula expressing the zonal harmonic $P_n(\theta)$ in terms of the Bessel functions $J_0(z)$ and $J_1(z)$ has been given by Lord Rayleigh, viz.,—

$$P_n(\theta) = J_0(z) + \frac{1}{12a^2} \{z^2 J_0(z) - 2z J_1(z)\},$$

where $z = a\theta$ and $a^2 = n(n+1)$, which is specially applicable when n is large and θ is small. Further terms in the coefficients of J_0 and J_1 have been found, requiring the evaluation of integrals involving Bessel functions:—

$$\int x^{2n} J_0 J_1 dx \quad \text{and} \quad \int x^{2n+1} J_1^2 dx + 2n \int x^{2n} J_1 dx.$$

In its extended form:—

$$P_n(\theta) = \left(\alpha + \frac{\beta}{a^2} + \frac{\gamma}{a^4} + \dots \right) J_0(z) - \left(\alpha^1 + \frac{\beta^1}{a^2} + \frac{\gamma^1}{a^4} + \dots \right) \frac{\theta}{6a} J_1(z).$$

Tables of the coefficients, α , β , γ , &c., which are functions of θ only, have been calculated to give the values of $P_n(\theta)$ to six decimal places for each angle of the quadrant. The formula can be employed even when the order n of the function is comparatively small and the argument θ as great as $\frac{1}{2}\pi$.

NOTICES OF BOOKS

A Manual of Chemistry. By ARTHUR P. LUFF, M.D., B.Sc., F.R.C.P.Lond., F.I.C., and HUGH C. H. CANDY, B.A., B.Sc.Lond., F.I.C. Sixth Edition, enlarged. London, New York, Toronto, and Melbourne: Cassell and Company, Ltd. 1918. Pp. xix.+745. Price 12s. net.

THERE can be no doubt that the medical student derives great advantage from the use of a book on chemistry which has been specially written to meet his requirements, and of such works this is one of the very best and most appreciated, as may be gathered from the number of editions through which it has passed. All the chemistry, inorganic and organic, theoretical and practical, which the student requires for the First Professional and First and Second M.B. Examinations is included, and it will be a great convenience to have it all brought together in one volume, which although much enlarged is still quite moderate in size. A sound general knowledge of the elements of chemistry could be obtained from the book, and the authors have taken special care to give the student an insight into fundamental principles while keeping well in view his particular requirements. In the sixth edition much more organic chemistry has had to be included than heretofore, and the sections on the sugars, cyanogen, urea, uric acid, and amino acids have been considerably extended. More practical work is also described, and all that prescribed for the First Professional and First and Second (Part 1.) M.B. Examinations is fully covered.

BOOKS RECEIVED.

"Van Nostrand's Chemical Annual." A Handbook of Useful Data for Analytical, Manufacturing, and Investigating Chemists, Chemical Engineers, and Students. Fourth Issue, 1918. Thoroughly Revised and Enlarged. Edited by JOHN C. OLSEN, A.M., Ph.D. Pp. xiii+778. London: Constable and Co., 10, Orange Street, Leicester Square, W.C. 15s. net.

NOTES.

THE funeral of Sir WILLIAM CROOKES took place on Thursday last, April 10. A service at St. John's Church, Notting Hill, was conducted by the Rev. H. Mackean. The chief mourners were Mr. and Mrs. Bernard Crookes, Mr. Walter S. Crookes, Mr. and Mrs. L. P. Crookes, Mr. and Mrs. A. J. Cowland, Mrs. Henry Crookes, Mr. Charles Crookes, and the grandchildren, Miss Enid, daughter of the late Joseph Crookes, and Master Willie Crookes, the son of Mr. L. P. Crookes. The congregation included representatives of all the learned Societies in London, personal friends of Sir William. Among those present were Sir Joseph Thomson, O.M. (Master of Trinity College, Cambridge, representing the Royal Society), the Hon. R. Clere Parsons (representing the Royal Institution of Great Britain), Sir Boverton Redwood (representing the British Science Guild), Prof. John Perry (representing the British Association), Sir Herbert Jackson (President of and representing the Institute of Chemistry), Mr. W. M. Mordey (representing the Institute of Electrical Engineers), Sir William Tilden, Sir Lawrence Jones (representing the Society of Psychological Research), Prof. Frank Clowes, D.Sc. (past President of and representing the Society of Chemical Industry), Dr. Alex. Scott (Vice-president of and representing the Chemical Society), Mr. W. F. Reid (chairman of the Institute of Inventors), Sir David Prain, Sir J. Larmor, M.P., Sir William Davison (Mayor of Kensington), Dr. Abraham Wallace, Dr. Francis Fox, Lady and Miss Macdonell, Dr. Donald Hood, Dr. Emerson Reynolds, Dr. and Mrs. Henry Armstrong, Sir John Snell, Prof. A. Schuster, and a number of representatives of the Notting-hill Electric Lighting Company. After the service at the church the members of the family proceeded to the Brompton Cemetery, where a further short service was held, and the body of Sir William was deposited in the family grave beside that of Lady Crookes, who died in May, 1916.

THE BRITISH SCIENCE GUILD has decided to organise an Exhibition in July and August on the lines of those held last year in London and Manchester. This year's exhibition will be on a much larger scale and will be held at the Central Hall, Westminster. The objects of the Exhibition are to illustrate recent progress in British Science and Invention and to help the establishment and development of new British industries, and will deal with the following subjects:—Agriculture, Aircraft, Chemistry, Education, Electrical Apparatus, Engineering Fuels, Medicine and Surgery, Metallurgy, Paper—Illustration and Typography, Physics, and Textiles. Each Section will be under the management of a Committee. Chemistry will receive special attention. The committee appointed for this section is as follows:—Walter F. Reid (Chairman); E. F. Armstrong, D.Sc.; J. C. Cain, D.Sc.; J. H. Gardiner; C. A. Keane, D.Sc.; Robert Mond; Prof. J. C. Philip, D.Sc. The Exhibition will enable new machines, appliances, and devices to be displayed before a large public. It will thus provide inventors with an opportunity of demonstrating the products of their ingenuity, and progressive manufacturers with a place to show the uses they have made of science and invention in new, or the development of old, industries. It is intended to publish a descriptive catalogue of exhibits similar to that issued last year and containing articles upon matters relating to scientific and industrial research of interest to manufacturers. Arrangements are also being made for the delivery of lectures upon important lines of progress, and several conferences will be held with the view of promoting exchange of views between makers and users, and scientific workers and industrialists. Demonstrations and the exhibition of cinematograph films of scientific and technical interest will be given daily, and as many as possible of the machines and accessories will be shown in action.

Mr. GEORGE HUBBARD, F.S.A., F.R.I.B.A., speaking at the Royal Institute of British Architects on February 3, on the Construction of a Dew-pond, described how it was possible to obtain a water supply in the absence of springs, rivers, and rain. At the outset he explained that the atmosphere which was warmed during the day was capable of containing a greater percentage of aqueous vapour than it could retain if it were chilled below the dewpoint during the night. The deposition of the aqueous vapour took place freely upon a condensing surface thermally isolated from the earth by a good non-conductor of heat. He referred to the ancient dew-ponds which formed the water supply to Neolithic man in his settlements on the hill tops, and to natural dew-ponds in the Colesberg district of Cape Colony, where, in the absence of springs, streams, and rains, ponds have a higher water level in the morning than they had in the previous evening. Mr. Hubbard proceeded to explain how he and his brother constructed a dew-pond in a very low-lying piece of land to test the question as to whether it would be possible to obtain a water supply even under unfavourable conditions in the absence of rain, springs, or streams. They began by excavating the earth over an area of 100 ft. square to a depth of 1 ft. 6 in.; over this they laid a bed of 4 in. of cement concrete and thickly coated the surface of this with pitch. The surface of the pitch was then spread over with fine sand, and mica slabs 2 ft. square and 2 in. thick were laid in regular order on top of the sand; about an inch space was left around each slab. In order to keep these slabs quite dry and so preserve their heat non-conducting property, the whole surface of the pond was covered with $\frac{3}{4}$ in. of asphalt. The asphalt ran into spaces between the slabs, but when it was completed it represented an even black appearance over the whole pond. At an early hour on an autumn morning, after a rainless night, the pond presented an extraordinary appearance. The whole surface looked like a chess-board with some 2500 perfect white squares all ruled off regularly by hard pitchblack lines about 1 in. wide between them. There was very little dew on the grass around the pond, but in the pond, immediately above each mica square, tall white hoar frost was standing, but there was not a trace of hoar frost on the asphalt above the joints, which stood out as hard black lines. In a few hours the sun melted the hoar frost, and hundreds, if not thousands, of gallons of water lay in great pools and puddles on the surface of the pond. It was a comparatively warm day, and the asphalt, protected as it was by the mica slabs, retained the heat, and the sun in the course of the day dried up the pond.

A VERY simple method of estimation of the quantity of dew deposited naturally on grass is described in the *Meteorologische Zeitschrift*, xxxv., 48, by Dr. V. Parchinger, who places a sheet of blotting-paper on the grass to absorb the dew and subsequently determines its increase of weight. The highest value mentioned for the dew-fall is 0.17 mm.

DIAMONDS are, in value, far and away the most important product of South-West Africa, though the best deposits in which they are found are rapidly being worked out. The gravel which contains them lies in a strip along the coast, and no stones have been discovered more than fifteen miles from the sea. The deposits were first made known in April, 1908, and were so actively exploited during subsequent years that in 1913 they yielded over 20 per cent in value of the total diamond output of the world. The yield for that year was 1,284,727 carats, valued at £2,698,500. During 1914 the production of 1913 was left far behind. Up to August, 1914, 5,400,000 carats had been recovered, valued at nine and a quarter millions sterling. The average size of the stones increases steadily from north to south until it reaches a maximum in the Pomona area. The diamonds are quite unlike those washed from the blue ground of Kimberley or the Transvaal. In hardness and brilliancy they resemble Brazilian stones, and though small in size show a quality uniformly

good. The largest stone discovered by the Germans was 34½ carats; the average size varies from a fifth to a sixth of a carat. The layers of diamond-bearing gravel are usually from 4 to 6 inches thick, but between Luderitz Bay and Elizabeth Bay they sometimes extend to 25 and even 30 feet. In the rich holdings of Ida Tal, Pomona district, the gravel has yielded 200 carats per cubic metre at a working cost of 2s. 2d. per carat. In the poorer and more distant workings the cost has run up to 35s. a carat. Before the war the diamond industry employed some 500 whites and 5000 coloured labourers (Cape Boys and Ovambos). The richest and most accessible deposits have already been worked out, and although the recovery of diamonds is considered likely to continue for some time to come, the "life" of the fields was not expected by the Germans to extend beyond twelve or fifteen years. No important new areas have been discovered since 1910, though prospecting has been vigorously pursued. The German Government of the Protectorate controlled the sale of diamonds through the Diamanten-Régie, formed in 1900, and in 1914 definite quota was assigned to the individual mining companies. The purpose was to keep the market steady, to maintain profits, and to encourage development. The profits made by companies which secured rich holdings were almost beyond belief. The Koloniale Bergbau-Gesellschaft during the four years 1910 to 1913 distributed dividends amounting in the aggregate to 112 times its capital of £5025. These dividends, of which the highest was 3800 per cent for 1912, were distributed after meeting the heavy Government taxes.—*Board of Trade Journal*.

GERMAN trading interests are already making arrangements for the importation into the United States of German and Austrian china and earthenware. According to information from an authoritative source, interviews have taken place in New York to arrange for the handling of these goods. Their view is that there will be a considerable market for them here if they can be bought at a cheaper price than English, Japanese, or domestic goods. It is reported that one German agent has already made plans to obtain a large quantity of china, and that the goods will be marked "Made in Bohemia" or "Made in Bavaria," as it is believed that the buying public can easily be persuaded that neither of those countries was responsible for German aggression.—*Board of Trade Journal*.

DURING the war the manufacture of paper underwear received special attention in Germany, and it is reported that very considerable advance was made. Paper garments are said to have been produced that were soft to the touch and could be washed repeatedly without deterioration.

WE are glad to announce that Messrs. Ilford, Ltd., the well-known photographic plate makers, have been able to greatly reduce the prices of their plates, and that they are no longer asking for the return of old negative glasses.

S. AND A. GALBRAITH, Manufacturers and Merchants, Kyle Factory, Cumnock, desire to get into touch with publications dealings with preserve and sugar-boiling trades.

NOTES FROM FOREIGN SOURCES

Chlorine Index as a Comparative Measure of the Richness of Soils in Humus.—L. Lapique and E. Barbé.—The authors have shown that when sodium hypochlorite (Eau de Javel) acts on arable soils it loses active chlorine in proportions which vary within very wide limits. This effect is a measure of the amount of humus in the soil, and a method of classifying soils in the order of their richness in humus may be based upon it. This method, of which the details are given, has the advantage

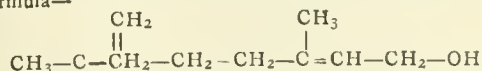
of being very rapid, and the process can be carried out on the spot.—*Comptes Rendus*, clxviii., No. 2.

Method of Rapid Reduction of Potassium Chloroplatinate.—M. Horsch.—In all methods of determining potassium by the reduction of potassium chloroplatinate the platinum is weighed in the form of powder, and has to be washed, filtered, dried, and ignited with the filter, which involves waste of time and probable loss of material. The new method described by the author is very rapid and simple, and gives satisfactory results. The salt is dissolved in boiling water, alcohol is added, and the solution is evaporated to dryness in a platinum crucible over a water-bath. The metallic platinum then forms a coherent and uniform film on the walls of the crucible. Formaldehyde effects the same reduction, but the film does not adhere completely and the process is less rapid.—*Comptes Rendus*, clxviii., No. 3.

Constitution of Nitrous Fumes.—P. Jolibois and A. Sanfourche.—If air and nitric oxide are mixed in the proportions necessary to make N_2O_3 combination is instantaneous; at the end of one-tenth second the reaction is complete. After 100 seconds contact no nitric compounds are formed, showing that gaseous N_2O_3 is not dissociated in these conditions. If air and nitric oxide are mixed in the proportions necessary to form NO_2 the N_2O_3 stage is very rapidly reached. After one second no appreciable amount of NO_2 is formed, while after 100 seconds the transformation is almost totally effected.—*Comptes Rendus*, clxviii. No. 4.

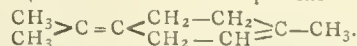
α - and β -Oxydihydrocinchonines and their Role in the Production of certain Isomers of Cinchonine.—E. Léger.—The author has previously shown that α -oxy-cinchonine is really an oxydihydrocinchonine, resulting from the fixation of H_2O at the double bond of cinchonine. To find out whether the β isomer has the same origin he has studied the action of HBr and H_2SO_4 on it. Like the α derivative the so-called β -oxycinchonine did not yield a hydrobromo derivative containing an O more than cinchonine, but hydrobromocinchonine and hydrobromo apocinchonine. These two compounds were accompanied by isomers of cinchonine—cinchonigine, cinchoniline, apocinchonine, β cinchonine, and some unaltered β -oxycinchonine. When 50 per cent H_2SO_4 acts on the β isomer cinchoniline is the chief product, mixed with cinchonigine, and the same compounds are obtained with 70 per cent acid, the yields being increased. Thus the so-called β -oxycinchonine is really an addition product of H_2O and cinchonine. The α and β compounds are stereo isomers, and their rotatory powers differ only slightly.—*Comptes Rendus*, 1919, clxviii., 404.

Constitution of Geraniol, Linalool, and Nerol.—M. Verley.—The author believes that geraniol, which is easily obtained by reduction of citral, possesses the formula—



and corresponds to citronellol. Two distinct isomeric forms exist of the substances of the geranic series which are found in nature, i.e., geraniol, citral, linalool, and methylheptenone. The α form is much the most abundant; it is often accompanied by the β modification, but the latter occurs in small quantities only. Only very small amounts of nerol occur. Nerol or β citral accompanies citral in essence of lemongrass, and isolinalool is similarly associated with ordinary linalool. Dipentene is easily obtained directly from geraniol by loss of water and closing of the chain, a reaction which is readily brought about by the action of certain dehydrating agents such as formic acid. As geraniol is the oxygen derivative which is most widely distributed in natural essences, where limonene also occurs in great abundance, it is possible that these two compounds are derived from one another. The terpene which corresponds to nerol is the terpinolene

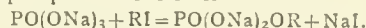
which is the β modification of the dipentene—



Like nerol this terpene is rare. It is spontaneously transformed into dipentene in the cold, and rapidly when warmed to 230° in presence of water.—*Bull. Soc. Chim. de France*, 1919, xxv.-xxvi., 68.

Researches on Molecular Transpositions of α -Glycols.—A. Orékhoff.—According to Werner's theory of valency the attractive force of an atom of carbon does not represent four distinct forces, pre-existent and oriented in space, but is a single force acting in all directions from the centre of the atom. Valency is only an empirical relation according to which atoms unite with one another; the total affinity of an atom may be regarded as constant, while the force of combination of the carbon atom with other atoms may vary within wide limits. This theory provides satisfactory explanations of the molecular transpositions of α glycols. Different radicals possess different "aptitude for migration" or "relative mobility." The nature of the migrating radical may be modified by the introduction of substituting radicals in the benzene nuclei. The nature of the dehydrating agent may have a considerable influence on the orientation of the transposition. The group $C_6H_5CH_2$ possesses a mobility and a saturation capacity less than the group C_6H_5 .—*Bull. Soc. Chim. de France*, 1919, xxv.-xxvi., 9.

Action of Alcoholic Iodides on Neutral Sodium Phosphate in Aqueous Solution.—Octave Bailly.—The alcoholic iodides react on neutral sodium phosphate in aqueous solution, giving, in the case of the first members of the series only, considerable proportions of the corresponding phosphoric mono ether—



The iodides of methyl, ethyl, allyl, propyl, isopropyl, and isobutyl were used, and deminormal aqueous solutions of trisodium phosphate. The temperature at which the reaction was carried out was 60° in the case of the iodides of methyl and allyl and 100° with the other iodides. The monoether was extracted, after elimination of the unattacked phosphate, in the form of the calcium salt which is very soluble even in the cold. A number of new alkyl phosphates of the alkalis and alkaline earths have thus been prepared. Besides the monoether there is always a small quantity of monophosphoric diether formed— $PO(ONa)_3 + 2RI = PO(OR)_2ONa + 2NaI$. The compounds obtained are really the phosphoric monoethers (alkylphosphates) and not the tautomeric bodies (alkylphosphinates) in which the alcoholic residue would be directly united with the phosphorus. The compounds are hydrolysable with regeneration of phosphoric acid. Generally speaking the solubility of the alkyl phosphates, derived from the monovalent alcohols, of the alkaline earth metals is greatest in the case of the barium salt, less for the strontium, and least for the calcium salt.—*Comptes Rendus*, 1919, clxviii., 560.

New Passage from the Fatty to the Aromatic Series.—I. Komninos.—When malonyl chloride acts on acetone in equimolecular proportions phloroglucine is produced, and at the same time a crystalline substance of formula $Cl.CO.CH_2.CO.CH_2.CO.CH_3$. This substance under the action of calcium carbonate loses HCl and is nearly quantitatively transformed into phloroglucine. The constitutional formula of the latter is justified by this synthesis. This research leads to a new synthetic method, based upon the condensation of the chlorides of acid radicals and ketones, and providing the simplest means of passing synthetically from the fatty to the aromatic series.—*Bull. Soc. Chim. de France*, 1918, xxiii.-xxiv., 449.

Detection and Determination of β -Nitroso-Naphthol.—P. Nicolardot and L. Valli-Douan.—In view of the price of β -nitroso-naphthol it is important to be able to determine it by an accurate method, as commercial products may contain various impurities (unattacked

naphthol, various isomers, &c.). When to an acetone solution of β -nitroso-naphthol a titrated solution of a ferric salt is added, the complex $(C_{10}H_6ONO)_3Fe$, in which the iron is masked, is formed. When all the β -nitroso-naphthol has been converted into complex an excess of ferric salt is revealed by a drop of ammonium sulphocyanide. The method can be made rigorously quantitative by adding to the acetone solution of β -nitroso-naphthol an excess of about 10 cc. of titrated ferric salt and 50 cc. of distilled water, shaking for two minutes, and then allowing to stand till the next day. The precipitate then settles, and can be filtered off through a double filter paper. After having been washed it is dried at 70° to constant weight. The molecular weight of β -nitroso-naphthol is 173 and that of the ferric complex is 572. The factor is therefore $\frac{3 \times 173}{572} = 0.907$.—*Bull. Soc. Chim. de*

France, 1918, xxiii.-xxiv., 455.

Reduction Products of Oxymethylene Camphor.—H. Rupe, A. Akermann, and H. Takagi.—When oxymethylene is reduced with hydrogen in presence of nickel at the ordinary temperature and pressure, the chief product of the reaction is the keto-alcohol camphyl carbinol. From 80 to 95 per cent of the theoretical amount of this alcohol may be obtained, and 5 to 20 per cent of other substances, the chief of which is methylene camphor. The formation of this compound is due to the abstraction of water by the nickel. The second by-product is methyl camphor, and the ethyl ethers of camphyl carbinol and of oxymethylene camphor are also formed. Although careful search was made there were no traces of a second stereo-isomeric form of camphyl carbinol.—*Helvetica Chimica Acta*, 1918, i., 452.

MISCELLANEOUS.

Royal Institution.—The following are the lecture arrangements at the Royal Institution, after Easter:—Prof. Arthur Keith, four lectures on "British Ethnology—The People of Wales and Ireland." Prof. W. H. Bragg, two lectures on "Listening under Water." Dr. H. S. Hele-Shaw, two lectures on "Clutches." Prof. Frederick Keeble, two lectures on "Intensive Cultivation." Sir Valentine Chirol, two lectures on "The Balkans." Prof. H. S. Foxwell, two lectures on "Chapters in the Psychology of Industry"—(1) "Fourier and other Pioneers in the Movement for the Humanising of Industry"; (2) "Modern Industrial Organization—where it fails to observe the humanities of Industry and the Results." Mr. J. Vells, two lectures (1). "Cæsar's Personal Character as seen in his Commentaries"; (2). "Cæsar as a General." Mr. Julius M. Price, two lectures on "The Italian Front." The Friday Evening Meetings, at 5.30 o'clock, will commence on May 2, when Prof. John W. Nicholson will deliver a Discourse on "Energy Distribution in Spectra." Succeeding Discourses will be given by Sir George Macsrtney, Dr. S. F. Harmer, Sir Alexander C. Mackenzie, Sir John Rose Bradford, and Prof. Sir Ernest Rutherford.

Relation of Dehydration to Agriculture.—G. C. Prescott (U.S. Dept. of Agriculture, Circular 126, January 25, 1919).—Drying has been known for hundreds of years, and is probably the oldest method of food preservation which the human race has employed. In this country it was used in the early colonial days for both animal and vegetable foods. Massachusetts colonists dried corn after it had been cooked, the product being known as samp. Fruits, and especially the apple, were also dried in considerable quantities. Along the coast the drying of fish became an important industry. In other parts of the country other vegetables and fruits and meat products were dried. Peas and sweet corn may be men-

tioned as examples of the former, while along the Pacific Coast the long sunny period lends itself particularly to the drying of prunes, raisins, and other fruits. In the arid regions of the interior the Indians, and later the early settlers, dried their beef or buffalo meat by cutting into thin strips and hanging up for sun and wind to remove the excess moisture, and sear over the outside with a protective coating which would prevent infection and spoilage. This was known as jerked beef. The advantages of dehydration are almost too obvious to require extended statement. Most evident of all is the loss in weight. Vegetables in common use contain from 60 to 95 per cent of water. The dehydrated product should contain from 5 to 10 per cent of water. There is therefore a very large reduction in weight and consequent saving in transportation charges, which are, in general, based upon weight. Similarly, there is a loss in bulk amounting from 50 to 80 per cent of the bulk of the raw material. From the standpoint of agriculture the greatest advantage of dehydration is in the stabilisation of crops and the conservation of materials. With dehydration the excess of the years of great yield can be stored up and made available in the following year when prices are higher and the crop much smaller. Another great advantage is in the conservation of food materials. It is estimated that over 50 per cent of the fruits and vegetables grown in this country never reach the consumer as a result of poor transportation facilities, irregularities in marketing, of other causes. A third factor of importance in relation of dehydration to agriculture lies in the better diversity of crops that can be secured, and as a result of this the greater variety available to poor and rich alike throughout the year.—*Journal Franklin Institute*, clxxvii., No. 3.

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PATENTS AND DESIGNS ACTS, 1907-1914.

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THE CHEMICAL NEWS

VOL. CXVIII., No. 3080.

THE ANALYSIS OF BRASS INGOTS FROM SWARF.

By R. H. DEAKIN, M.Sc.

THE following mode of analysis of brass made from swarf has been found accurate and speedy. The elements estimated are Cu, Zn, Pb, Sn, Fe, Al, Ni. The process of analysis is divided into four portions.

1. *Copper (varying from 55 to 70 per cent).*—By the usual iodometric thiosulphate process on 0.50 gm. of the alloy. The addition of 2 cc. 20 per cent sodium phosphate to the acetic solution prevents the iron present from reacting. The true end-point with these brassy is found to be the point at which the colour of the solution changes from reddish-brown (following the purple of starch-iodide) to pale buff, and when a further drop of N/10 sodium thiosulphate produces no further change in the colour of the bulk. Too high results are obtained if the end-point is gauged by the effect of a drop of thiosulphate falling on the surface. Abnormal copper figures are checked by the electrolytic deposition method.

11. *Zinc and Nickel (Zinc 30 to 45 per cent).*—The zinc is estimated by the volumetric ferrocyanide process after removal of the copper as cuprous thiocyanate. 1 gm. of the brass is dissolved in 10 cc. conc. HCl and 2 cc. conc. HNO₃. The HNO₃ is boiled off, and after dilution to 100 cc. the solution is made ammoniacal and then just acid with HCl. Sulphur dioxide is bubbled through the hot solution till the colour pales and 7 cc. 20 per cent ammonium thiocyanate are added. After a further passage of SO₂, and standing for one half hour in a warm place, the CuCN is filtered off through hard double papers, the precipitate being washed with aired water. (The CuCN, ignited direct in the gas muffle to Cu₂S with possibly some CuO, serves as a useful check on the volumetric copper).

10 cc. conc. H₂SO₄ are added to the filtrate, and after boiling a few minutes, 5 cc. HNO₃, which completes the destruction of the excess thiocyanate. The solution is then taken to fuming, diluted, lead sulphate filtered off, and to the filtrate 2 grms. NH₄Cl and excess NH₄OH added. From the hot solution the hydrates of Fe and Sn are filtered off and washed well with hot 5 per cent ammonia water containing ammonium chloride.

(Examination of these hydrates shows that with ordinary care not more than 0.03 per cent. zinc is lost at this stage).

The filtrate is boiled to remove excess ammonia, made acid with conc. HCl, and 5 cc. excess added. It is then titrated with a solution of potassium ferrocyanide (1 cc. = approx. 0.01 gm. Zn) after heating to boiling and with a bulk of 250 cc. The external end-point with uranium acetate is soon observed with accuracy once the operator has become familiar with the transient end-point which first appears.

In practice it was found unnecessary to filter off the lead sulphate, since if left in the solution it is partly removed as hydrate with the iron, and moreover what remains has no serious influence on the titration. Zinc foil and zinc oxide were found to contain lead and other impurities, so standardization of the ferrocyanide was finally achieved with pure atek zinc, observing identical conditions of acidity, &c., as with the samples.

Nickel, which is frequently present (trace 0.01, 0.06 per cent), is looked for after removal of the iron and excess

ammonia in the above process. It is precipitated as nickel oxime, filtered off, and estimated cyanometrically with N/50 solutions. The zinc solution is boiled down with HCl to destroy excess glyoxime before titrating. Care must be exercised that no zinc hydrate is left on the filter with the nickel oxime.

III. *Lead (up to 2.0 per cent).*—This is estimated by the familiar fuming process with sulphuric acid. The lead sulphate, dissolved in ammonium acetate, being finally precipitated as lead molybdate. With regard to the formation of acid lead molybdates the following is of interest:—

0.1199 gm. of pure lead nitrate (containing the amount of lead present in 5 grms. of a brass with 1.50 per cent. lead) gave—

(a). On adding 5 cc. of 5 per cent. ammonium molybdate, all at once, to the boiling ammonium acetate solution of the lead sulphate, a silky yellow precipitate which worked out at 1.57 per cent lead.

(b). On adding the ammonium molybdate drop by drop only (till as far as possible no further precipitate formed), a white granular precipitate, rapid to filter, and which worked out at 1.50 per cent lead. The ammonium molybdate must therefore be added drop by drop.

IV. *Tin (up to 1 per cent), Iron (up to 1 per cent), and Aluminium.*—The usual method of estimating tin in brassy, by isolation of metastannic acid with HNO₃, leads to contamination of the ignited SnO₂ with iron, if this element is present in the brass.

A method for tin, depending on the quantitative precipitation of the hydrate (Price and Mead, "Technical Analysis of Brassy," p. 216) has been tried and, after modification, found satisfactory. It has the advantage of leaving the iron in a reduced condition in solution. 5 grms. of the brass, after careful cleaning with a magnet, are dissolved in 40 cc. of a mixture of 3HCl (conc.), 1HNO₃ (conc.) After dilution to 200 cc., 2 grms. NH₄Cl and 40 cc. NH₄OH are added. The solution is brought to the boil and filtered through pulp and washed well with hot 5 per cent. ammonia water. The pad is extracted with hot 1:1 HCl and cold water back into the same beaker and reprecipitated with ammonia, filtered, and again washed with ammonia water. Then follows a second extraction, this time with cold 1:3 H₂SO₄, which leaves on the pad as sulphate any lead present. 5 cc. conc. H₂SO₄ are added to the extract, which is made up to a bulk of 500 cc., and through it when hot is passed a rapid stream of H₂S. When the solution is saturated it is allowed to stand on the edge of the hot plate till the tin sulphide coagulates and settles. The sulphide is filtered off through hard double pleated papers and washed with H₂S water containing a little sulphuric acid and ammonium acetate. It is then dried, ignited, treated with a little powdered ammonium carbonate, ignited further, and weighed as SnO₂.

Slight contamination with copper and lead occurs and was found by analysis of the ignited SnO₂ from 20 estimations to give an average error of 0.007 per cent Sn (with average 0.3 per cent Sn present). This, however, can be much diminished by exercising greater care in washing out the copper with ammonia water and by using a substantial pad and cold 1:3 H₂SO₄ for the second extraction of the hydrates. The filtrate from the tin sulphide is collected in an Erlenmeyer flask (600 cc.). A filter grate is introduced and the solution is boiled and repeatedly tested with moistened lead acetate paper, held over the mouth of the flask, till no H₂S remains. Thirty minutes boiling is usually sufficient, the bulk after that time being about 250 cc. After rapid cooling, the reduced iron is titrated with N/10 potassium permanganate.

The following figures show that complete reduction, removal of H₂S, and no reoxidation take place. Four portions (0.050 gm.) of iron wire were weighed out. Two were dissolved in 10 per cent H₂SO₄ in Erlenmeyer flasks with Bunsen valves, cooled, and titrated with N/10 approx.

KMnO_4 . They required 8.40 and 8.45 cc. to oxidise them. The other two were dissolved in HNO_3 , and the hydrate, precipitated with ammonia, filtered off and extracted with 50 cc. 1:2 cold H_2SO_4 . The extract was made up to a bulk of 300 cc., heated to boiling, and H_2S passed for a quarter of an hour. The sulphur was filtered off, 5 conc. H_2SO_4 added, and the H_2S boiled off in 25 minutes. After cooling the solutions were titrated. Both required 8.40 cc. KMnO_4 .

With known added amounts of tin and iron, together with copper and zinc, as in 5 grms. of a typical brass, the following figures were obtained by this process:—

Sn added	Sn found	Fe added	Fe found
Per cent.	Per cent.	Per cent.	Per cent.
0.65	0.64	0.25	0.25
0.27	0.28	0.45	0.45

When it is required to examine the brass for aluminium the filtrate from the tin sulphide is boiled free of H_2S , oxidised with a few cc. of HNO_3 (titration at this stage would introduce manganese, which is best avoided), and the iron and aluminium precipitated as hydrates with ammonia and extracted into excess 30 per cent NaOH with HCl . The iron thrown out is filtered off and estimated as above or gravimetrically. The NaOH solution is made acid with HCl , and the aluminium, after a double precipitation with slight excess ammonia to remove sodium chloride, is ignited to Al_2O_3 . Where much tin is present (0.5 per cent or more) a small amount may not be removed as sulphide and will contaminate the Al_2O_3 . It can be removed with H_2S before the final precipitation of the aluminium. A blank on the reagents used is essential. Traces only of manganese (0.002 per cent) and bismuth (0.0005 per cent), also arsenic up to 0.03 per cent, are found to occur in these brasses.

MEASUREMENTS OF WAVE-LENGTHS IN THE SPECTRUM OF NEON.

By KEVIN BURNS, W. F. MEGGERS, and P. W. MERRILL.

THE lines in the neon spectrum are very sharp, a quality which recommends this gas as a standard source wherever the lines have sufficient strength. The ultra-violet group between 3369 Å and 3520 Å may be used for standards, and there are a few good infra-red lines, but the strength and distribution of the lines in the region 5852 Å to 7438 Å make the neon spectrum particularly useful as a comparison in this region.

The wave-lengths of fifty-five lines in the neon spectrum have been measured by means of the interferometer. These lines lie in the region 3369 Å to 8495 Å. The strong lines in the visible region of the spectrum have been observed with great accuracy, the probable error being one part in several millions, or less than one-tenth the width of the line. These strong lines were observed by means of three different pairs of interferometer plates which were each used on several interferometers. The ultra-violet lines and all the strong lines in the visible were compared directly with the fundamental standard 6438 Å. Some of the deep red and infra-red lines were compared with well-determined lines in the visible neon spectrum.

One hundred and eighty-nine faint lines in the visible and infra-red neon spectrum have been measured by means of a concave grating. The probable error of these grating measurements is one or two hundredths Angstrom. The region covered by the grating observations extends from 5343 Å to 8783 Å.

The constant differences discovered by Watson are found to hold with remarkable exactness in the case of lines which are strong enough to be measured with the highest accuracy. In fact, the differences are exactly constant within the limits set by the accuracy of the wave-lengths.—*Bur. Stands. Sci. Paper No. 329, 1918, p. 10.*

PHYSICAL CHEMISTRY AND ITS BEARING ON THE CHEMICAL AND ALLIED INDUSTRIES.*

By Prof. JAMES C. PHILIP, O.B.E., M.A., Ph.D., D.Sc.

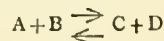
IN the first lecture an attempt was made, more especially in connection with sulphuric acid manufacture and the production of synthetic ammonia, to demonstrate the value of certain physico-chemical principles as applied to technology. These principles provide a rational basis for the investigation of processes in which questions of chemical equilibrium are involved; they permit a concise formulation of the influence of various important factors, and render possible a real scientific control of such operations when they reach the manufacturing stage.

Exact knowledge, however, of the equilibrium conditions prevailing in such technical gas reactions as those already considered does not suffice for the practical manufacturer. For obvious economic reasons he must raise a question as to the *velocity* of the particular reaction concerned. However favourable the position of equilibrium may be with regard to the desired product, the reaction is of no value from the technical standpoint, unless the attainment of equilibrium is, or can be made, reasonably rapid.

Now the velocity of a chemical reaction, as is well known, can be increased by raising the temperature, but this may involve, as in the instances of the sulphuric acid contact process and the ammonia synthesis, an undesirable shifting of the equilibrium, and consequently a diminished yield of the product. A high yield and rapid completion of the reaction may not both be realisable along these lines.

In addition, however, to rise of temperature there is another recognised method of accelerating a chemical reaction, namely, by the use of "catalysts." These are substances the mere presence of which in contact with the reacting system promotes the change and hastens the establishment of equilibrium. Chemical literature has long recorded observations of a general kind relating to the action of catalysts, but a rational study of their influence and their efficiency can be attempted only on physico-chemical lines. In indicating what these lines are it is desirable to recall the way in which the physical chemist arrives at a quantitative expression for the rate of a chemical reaction.

The application of kinetic conceptions to a reversible gaseous reaction, as discussed in the first lecture, leads to the view that progress towards equilibrium, i.e., the net velocity of the change, is determined by the velocities of two opposed component reactions. Thus, if—



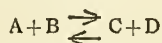
represents the reversible reaction, v_1 the velocity of the change $A + B \rightarrow C + D$, v_2 that of the change $C + D \rightarrow A + B$, and a, b, c, d the concentrations at the moment of the four molecular species involved, then the net velocity of the reaction is given by $V = v_1 - v_2 = k_1ab - k_2cd$. If now it is supposed that the reaction begins with A and B alone present in the concentrations a_0 and b_0 , and that after an interval of time t from the start, the concentrations of C and D are both x , the velocity formula becomes $V = k_1(a_0 - x)(b_0 - x) - k_2x^2$. In the language of the differential calculus $V = \frac{dx}{dt}$, and the progress of this reversible reaction towards equilibrium is therefore represented by the equation—

$$\frac{dx}{dt} = k_1(a_0 - x)(b_0 - x) - k_2x^2,$$

* Caquot Lecture (II.). Delivered before the Royal Society of Arts, December 9, 1918. From the *Proceedings of the Royal Society of Arts*, LXVII., No. 3431.

where k_1 and k_2 are so-called velocity coefficients, the numerical values of which are a quantitative expression of the rates of the forward and the back reaction respectively.

In cases where the position of equilibrium in the reversible reaction—



lies practically at the right-hand extreme, the velocity of the back reaction becomes negligible, and the velocity equation may be written $\frac{dx}{dt} = k_1(a_0 - x)(b_0 - x)$, or simply

$\frac{dx}{dt} = k(a_0 - x)(b_0 - x)$. Integration of this equation leads to the formula—

$$k = \frac{1}{(a_0 - b_0)t} \cdot \log_e \frac{b_0(a_0 - x)}{a_0(b_0 - x)}$$

and if in any particular case the progress of the change can be followed experimentally, *i.e.*, if the values of x corresponding with various values of t can be ascertained, then k can be calculated, and the velocity of reaction at the temperature of experiment is quantitatively expressed thereby. In numerous cases the law of mass action, as embodied in the foregoing expression for k , has been verified experimentally; x , the amount of change in time t , varies with t in such a manner that—

$$\frac{1}{(a_0 - b_0)t} \cdot \log_e \frac{b_0(a_0 - x)}{a_0(b_0 - x)}$$

remains constant.

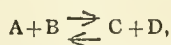
As an illustration of the extent to which these requirements of the law of mass action are fulfilled in an individual instance the saponification of ethyl acetate by an equivalent amount of sodium hydroxide may be taken. This is a time reaction, the course of which may be followed by extracting samples of the reaction mixture from time to time and titrating for the residual alkali; the quantity of this naturally falls off as the change proceeds. In Table I. the figures for a particular experiment are recorded, those in the first column representing the intervals from the start at which samples were extracted, those in the second column giving the relative alkalinity of each sample (alkalinity of initial mixture = 1.00), and those in the last column giving the calculated values of the velocity coefficient.

TABLE I.—Saponification of Ethyl Acetate by Sodium Hydroxide.

Minutes from start.	Relative alkalinity.	Velocity coefficient.
4	0.659	0.129
6	0.570	0.126
8	0.487	0.132
10	0.437	0.129
12	0.388	0.131
15	0.341	0.129
20	0.276	0.131

The satisfactory constancy of the figures in the last column demonstrates the applicability of the law of mass action in this case.

In the reaction—



which has been taken as the basis of the argument, two molecules undergo change of concentration as the reaction proceeds, and the velocity coefficient k is accordingly described as the constant for a "bimolecular" reaction. On the same lines as those already followed an expression can be obtained for the velocity coefficient of a "unimolecular" reaction, in which only one kind of molecule undergoes change of concentration; for this case it

is found that $k = \frac{1}{t} \cdot \log_e \frac{a}{a-x}$, in which expression a

is the initial concentration of the substance undergoing change, and x is its concentration after time t from the start. Where more than two molecules undergo change of concentration, *i.e.*, for reactions of a higher "order" than the second, more complicated expressions are obtained for the velocity coefficient.

With these definite methods for expressing quantitatively the velocity of a chemical reaction at any given temperature, it becomes possible to state the influence of various factors on the velocity by recording the corresponding change in the velocity coefficients. In reference, for example, to the influence of temperature on the rate of a chemical change it is customary to represent this effect by a statement of the increase in k for a temperature interval of 10° ; *i.e.*, by recording the value of the ratio $\frac{k_{T+10}}{k_T}$. The study of a very large number of cases has

shown that for homogeneous changes, where the reaction system is entirely gaseous or entirely liquid, the value of $\frac{k_{T+10}}{k_T}$ lies, as a rule, between 2 and 3, the velocity being doubled or trebled for a rise of 10°C.

As with temperature so with other factors which affect the rate of chemical change, the velocity coefficient provides a quantitative basis for their assessment. In relation to catalysis, in particular, it becomes possible to state the efficiency of one and the same catalyst at different concentrations, to determine whether the activity of the catalyst remains constant, and to compare the influence of different catalysts under given conditions.

Before proceeding to develop these considerations it is desirable to state definitely what are the characteristics of a catalyst from the physico-chemical point of view. One of the main facts about a catalyst is that its quantity may be, and often is, exceedingly small in comparison with the quantities of the reacting substances which are affected. It has been stated, for example, that in the Schröder-Grillo process for the production of sulphuric acid, in which process the contact mass consists of finely-divided platinum on magnesium sulphate, 5 grms. of platinum are sufficient for an output of one ton of oleum per day, with a loss of only 20 mgrms. platinum. It appears also, to take an example in another field, from information supplied to the writer by Mr. Maxted, that in the synthesis of ammonia with an iron-potash catalyst, an output of something like two tons of ammonia per litre of catalyst space can be obtained before it is necessary to change the catalyst.

Further, in normal circumstances the activity of the catalyst remains unimpaired when the reaction which it has accelerated is at an end. An interesting illustration of this characteristic of catalysts is furnished by Bredig's experiments on the influence of colloidal platinum in promoting the combination of hydrogen and oxygen at ordinary temperatures. In one case 2.5 cubic cm. of colloidal platinum solution (containing 0.17 mgrm. of the metal) were shaken with electrolytic gas, and the decrease in the volume of the gas, due to the combination of hydrogen and oxygen, was determined at ten-minute intervals. Table II. gives the results obtained.

TABLE II.

Time in minutes	Decrease in the gas volume. Cc	Decrease per minute.
10	17.8	1.78
20	35.8	1.80
30	54.8	1.90
40	72.4	1.76
50	90.2	1.78

The figures in the last column of Table II. afford no evidence of any decrease in the activity of the colloidal

platinum as the reaction proceeds. Further, the same colloidal platinum was shaken intermittently for fourteen days with the hydrogen+oxygen mixture, about 10 litres of which were converted to water in this interval. Not only is the contrast between the minute quantity of the catalyst and the extent of the induced change sufficiently striking, but it was found at the end of the fourteen days that the rate of decrease of the gas volume, measured over successive ten-minute intervals with constant shaking, as at the beginning of the experiment, was 2.02, 1.87, 1.95, 1.97, and 2.01 cubic cm. per minute. Plainly, the catalytic efficiency of the platinum is no lower at the end of the experiment than at the commencement.

Now, in the technical applications of catalysis one of the most serious problems has been precisely how to keep the catalyst in a state of unimpaired efficiency. However active the contact substance may be at the start, it is useless from the technical standpoint unless it has a reasonably long life. This difficulty does not arise with a dissolved catalyst, such as an acid in the hydrolysis of starch; but where the catalyst is a solid substance, when we are dealing with a case of so called "heterogeneous" catalysis, then the problem is a serious one. In many instances the technical development of a promising catalytic reaction has been held up by the difficulty of preserving the catalyst in its full activity. The catalyst deteriorates owing to the presence of some foreign substance, or "poison," in the materials which are reacting under the influence of the catalyst.

A notable example of this difficulty is furnished by the history of the development of the sulphuric acid contact process. So long as absolutely pure gases are employed it appears that the platinum catalyst maintains its efficiency. In one case which has been put on record, where sulphur dioxide, obtained by the evaporation of the liquid substance, was mixed with filtered air and passed over the contact mass a 95 per cent yield of sulphur trioxide was still given by platinised asbestos which had been in the plant for about ten years continuously without renewal. It is a fair inference that the catalytic action of platinum continues indefinitely if pure gases are employed.

The record, however, of the prolonged efforts of the Badische Anilin- und Soda-Fabrik to utilise for the purpose of the sulphuric acid contact process the gases obtained by roasting blende or pyrites demonstrates the extreme sensitiveness of the platinum catalyst to impurities. It was found that even when the pyrites gases were cooled by passage through long metal pipes, repeatedly scrubbed with sulphuric acid, and finally filtered through dry coke and asbestos, the contact mass gradually became less effective, and finally lost its power altogether. The discovery was made that certain substances, notably arsenic, are specially injurious to the catalytic efficiency of platinum, and further investigation showed that even the drastic purification just described had failed to remove the last traces of arsenic from the pyrites gases.

The sulphuric acid "mist" or "fume" in these gases is extraordinarily persistent, and apparently is the carrier of the arsenic. The removal from a stream of gas of those impurities which are in a very finely-divided liquid or solid condition is recognised as sometimes a more difficult operation than the absorption of gaseous impurities by chemical means. In the case of the sulphuric acid contact process it was only after much patient labour that means were found, including slow cooling, thorough scrubbing, and wet filtration, for removing all traces of "poisons" from the pyrites gases. During the last few years a novel method of dealing with all sorts of mist and fume has been introduced by Cottrell, based on the fact that a strong electrical field promotes the settlement and precipitation of suspended particles. Numerous plants involving this principle have been designed and erected, more particularly in connection with smelting works and blast-furnaces, and the same process is being applied for the removal of the mist from the pyrites gases employed in the sulphuric acid manufacture.

The serious difficulties encountered in using pyrites gases in the sulphuric acid contact process gave some support to the belief that the poisoning of the catalyst was inevitable, and it was accordingly suggested that the platinum should be deposited on a soluble carrier, so that when the contact substance lost its efficiency the valuable metal could be recovered quite easily by appropriate treatment. This was the method employed in the Schröder-Grillo process, a very active catalyst being prepared by soaking magnesium sulphate in the solution of a platinum salt, and then heating in the presence of sulphur dioxide; when the contact mass has been formed the platinum is about 0.1 per cent of the whole.

The fact that the amount of a catalyst may be almost infinitely small compared with the quantities of the substances which react under its influence makes it extremely probable that the final state of the reactive system must be independent of the catalyst. This would mean, for a reversible reaction in particular, that the state of equilibrium finally attained will be the same whether the catalyst is there or not. The true catalyst, that is, will influence only the rate at which equilibrium is established, not the position of equilibrium itself, or the energy change accompanying the reaction. The catalyst may be compared to the oil which facilitates the sliding of a weight down an inclined plane, without affecting the total energy derivable from the fall of the weight.

Illustrative confirmation of this important conclusion is furnished by Turbaba's work on the equilibrium between acetaldehyde and paraldehyde. The equilibrium mixture of these two substances at 50.5° contains 33.9 per cent of acetaldehyde and 66.1 per cent of paraldehyde, and the conversion of paraldehyde into this mixture is accompanied by a marked and easily measurable increase of volume. The change is accelerated by a variety of substances, but it was found that with different catalysts in varying quantity the difference in volume of the paraldehyde and the equilibrium mixture is practically the same in every case, as is shown in Table III.

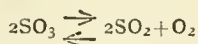
TABLE III.—Paraldehyde $\rightleftharpoons$ Acetaldehyde.

Catalyst.	Per cent. Catalyst.	Percentage increase of volume.
Sulphur dioxide ..	0.08	8.20
Sulphur dioxide ..	0.002	8.19
Zinc sulphate ..	2.7	8.13
Hydrochloric acid ..	0.13	8.13
Oxalic acid ..	0.52	8.27
Phosphoric acid ..	0.54	8.10

Clearly, the percentage increase of volume is independent of the particular catalyst employed, and, in the case of sulphur dioxide, independent also of the amount of catalyst. In this case, then, and in fact for all truly catalytic reversible reactions, the catalyst affects only the velocity of the change, not the composition of the equilibrium mixture. If this statement were not correct then the investigation of equilibrium reactions in presence of catalysts and the evaluation of equilibrium constants, as in the sulphuric acid contact process and the ammonia synthesis, would be an unjustifiable proceeding.

If now, in any reversible reaction the position of equilibrium is unaffected by the catalyst it follows that the value of the equilibrium constant K is unaltered. This constant, however, as was shown in the previous lecture, is the ratio of two velocity coefficients, k_1 and k_2 , which refer to the forward and the back reactions respectively. It follows therefore that k_1 and k_2 must be affected in an equal degree by the catalyst; that is, the catalyst accelerates the forward and the back reactions in the same proportion. The mere fact that iron and nickel promote the decomposition of ammonia at high temperatures suggested that these metals would act as catalysts for the opposed reaction also, viz., the union of nitrogen and hydrogen. This was found to be the case. Again, in the

absence of a catalyst, sulphur trioxide once formed appears to be remarkably stable at high temperatures, even where the equilibrium constant for the reaction—



would require a far-reaching decomposition into sulphur dioxide and oxygen. The rate of decomposition, no less than the rate of synthesis, is determined largely by the presence of an appropriate catalyst.

With these characteristics of catalysts in mind we may endeavour to apply the conceptions of reaction velocity and the formulæ embodying these conceptions for the purpose of a rational study of catalysis. The success which has attended the physical chemist's efforts along these lines has been much more notable in some directions than in others, and it has become clear that a distinction must be drawn between "homogeneous" catalysis on the one hand and "heterogeneous" catalysis on the other. In the former case the catalyst is in the same physical state (gaseous or liquid) as the substances which are reacting; in the latter the catalyst is solid, and cannot be in a condition of true homogeneous mixture with the reacting compounds.

(To be continued).

THE COLOUR OF WATER.*

By WILDER D. BANCROFT, Ph.D.,
Professor of Physical Chemistry, Cornell University.

THE literature on the colour of water is widely scattered; it appears not to have been read by anybody; and it is somewhat contradictory. It has, therefore, seemed desirable to collect the material in an accessible form as it constitutes an interesting chapter in the general subject of the colours of colloids.

Tyndall ("Fragments of Science: The Sky; Voyage to Algeria; Niagara") has discussed the blue colour of turbid media with special reference to the colour of the sky and of the sea. In Newton's rings the colour nearest to the central black spot is a faint blue—blue of the first order—corresponding to the film of air when thinnest.

"If a solid or liquid, of the thickness requisite to produce this colour, were broken into bits and scattered in the air, Newton inferred that the tiny fragments would display the blue colour. Tantamount to this, he considered, was the action of minute water-particles in the incipient stage of their condensation from aqueous vapour. Such particles suspended in our atmosphere ought, he supposed, to generate the serenest skies. Newton does not appear to have bestowed much thought upon this subject; for to produce the particular blue which he regarded as sky-blue, thin plates with parallel surfaces would be required. The notion that cloud-particles are hollow spheres, or vesicles, is prevalent on the Continent, but it never made any way among the scientific men of England. De Saussure thought that he had actually seen the cloud-vesicles, and Faraday, as I learnt from himself, believed that he had once confirmed the observation of the illustrious Alpine traveller. During my long acquaintance with the atmosphere of the Alps I have often sought for these aqueous bladders, but have never been able to find them. Clausius once published a profound essay on the colours of the sky. The assumption of small water drops, he proved, would lead to optical consequences entirely at variance with facts. For a time, therefore, he closed with the idea of vesicles, and endeavoured to deduce from them the blue of the firmament and the morning and evening red.

"It is not, however, necessary to invoke the blue of the first order to explain the colour of the sky; nor is it necessary to impose upon condensing vapour the difficult,

if not impossible, task of forming bladders, when it passes into the liquid condition. Let us examine the subject. Eau-de-Cologne is prepared by dissolving aromatic gums or resin in alcohol. Dropped into water, the scented liquid immediately produces a white cloudiness, due to the precipitation of the substances previously held in solution. The solid particles are, however, comparatively gross; but, by diminishing the quantity of the dissolved gum the precipitate may be made to consist of extremely minute particles. Brücke, for example, dissolved gum-mastic, in certain proportions, in alcohol, and carefully dropping his solution into a beaker of water, kept briskly stirred, he was able to reduce the precipitate to an extremely fine state of division. The particles of mastic can by no means be imagined as forming bladders. Still, against a dark ground—black velvet for example—the water that contains them shows a distinctly blue colour. The bluish colour of many liquids is produced in a similar manner. Thin milk is an example. Blue eyes are also said to be simply turbid media. The rocks over which glaciers pass are finely ground and pulverised by the ice, or the stony emery imbedded in it; and the river which issues from the snout of every glacier is laden with suspended matter. When such glacier water is placed in a tall glass jar, and the heavier particles are permitted to subside, the liquid column, when viewed against a dark background, has a decidedly bluish tinge. The exceptional blueness of the Lake of Geneva, which is fed with glacier water, may be due, in part, to particles small enough to remain suspended long after their larger and heavier companions have sunk to the bottom of the lake.

"We need not, however, resort to water for the production of the colour. We can liberate, in air, particles of a size capable of producing a blue as deep and pure as the azure of the firmament. In fact, artificial skies may be thus generated, which proves their brotherhood with the natural sky by exhibiting all its phenomena. There are certain chemical compounds—aggregates of molecules—the constituent atoms of which are readily shaken asunder by the impact of special waves of light. Probably, if not certainly, the atoms and the waves are so related to each other, as regards vibrating period, that the wave motion can accumulate until it becomes disruptive. A great number of substances might be mentioned whose vapours, when mixed with air and subjected to the action of a solar or an electric beam, are thus decomposed, the products of decomposition hanging as liquid or solid particles in the beam which generates them. And here I must appeal to the inner vision already spoken of. Remembering the different sizes of the waves of light, it is not difficult to see that our minute particles are larger with respect to some waves than to others. In the case of water, for example, a pebble will intercept and reflect a larger fractional part of a ripple than of a larger wave. We have now to imagine light-undulations of different dimensions, but all exceedingly minute, passing through air laden with extremely small particles. It is plain that such particles, though scattering portions of all the waves, will exert their most conspicuous action upon the smallest ones; and that the colour-sensation answering to the smallest waves—in other words, the colour line—will be predominant in the scattered light. This harmonises perfectly with what we observe in the firmament. The sky is blue, but the blue is not pure. On looking at the sky through a spectroscope, we observe all the colours of the spectrum; blue is merely the predominant colour. By means of our artificial skies we can take, as it were, the firmament in our hands and examine it at our leisure. Like the natural sky, the artificial one shows all the colours of the spectrum, but blue in excess. Mixing very small quantities of vapour with air, and bringing the decomposing luminous beam into action, we produce particles too small to shed any sensible light, but which may, and doubtless do, exert an action on the ultra-violet waves of the spectrum. We can watch these particles, or rather the space they occupy, till they grow to a size able to

* From the *Journal of the Franklin Institute*, clxxvii., No. 3.

TABLE I.

No.	Location.	Colour of Sea.	Appearance in Luminous Beam.
1.	Gibraltar Harbour	Green	Thick with fine particles.
2.	Two miles from Gibraltar	Clearer green	Thick with very fine particles.
3.	Off Cabreta Point	Bright green	Still thick, but less so.
4.	Off Cabreta Point	Black-indigo	Much less thick, very pure.
5.	Off Tarifa	Undecided	Thicker than No. 4.
6.	Beyond Tarifa	Cobalt blue	Much purer than No. 5.
7.	Twelve miles from Cadiz	Yellow-green	Very thick.
8.	Cadiz Harbour	Yellow-green	Exceedingly thick.
9.	Fourteen miles from Cadiz	Yellow-green	Thick, but less so.
10.	Fourteen miles from Cadiz	Bright green	Much less thick.
11.	Between Capes St. Mary and Vincent ..	Deep indigo	Very little matter, very pure.
12.	Off the Burlings	Strong green	Thick, with fine matter.
13.	Beyond the Burlings	Indigo	Very little matter, pure.
14.	Off Cape Finisterre	Undecided	Less pure.
15.	Bay of Biscay	Black-indigo	Very little matter, very pure.
16.	Bay of Biscay	Indigo	Very fine matter. Iridescent.
17.	Off Usbant	Dark green	A good deal of matter.
18.	Off St. Catherine	Yellow-green	Exceedingly thick.
19.	Spithead	Green	Exceedingly thick.

yield the firmament of azure. As the particles grow larger under the continued action of the light, the azure becomes less deep; while later on a milkiness, such as we often observe in nature, takes the place of the purer blue. Finally the particles become large enough to reflect all the light-waves, and then the suspended 'actinic cloud' diffuses white light. . . .

"In the harbour of Gibraltar, on the morning of our departure, I resumed a series of observations on the colour of the sea. On the way out a number of specimens had been collected, with a view of subsequent examinations. But the bottles were clear bottles, of doubtful purity. At Gibraltar, therefore, I purchased fifteen white glass bottles, with ground-glass stoppers, and at Cadiz, thanks to the friendly guidance of Mr. Cameron, I secured a dozen more. These seven and twenty bottles were filled with water, taken at different places between Oran and Spithead. And here let me express my warmest acknowledgments to Captain Henderson, the commander of H.M.S. *Urgent*, who aided me in my observations in every possible way. Indeed, my thanks are due to all the officers for their unflinching courtesy and help. The captain placed at my disposal his own coxswain, an intelligent fellow named Thorgood, who skillfully attached a cord to each bottle, weighted it with lead, cast it into the sea, and, after three successive rinsings, filled it under my own eyes. The contact of jugs, buckets, or other vessels was thus avoided; and even the necessity of pouring out the water, afterward, through the dirty London air.

"The mode of examination applied to these bottles has been already described. The liquid is illuminated by a powerfully condensed beam, its condition being revealed through the light scattered by its suspended particles. Care is taken to defend the eye from the access of all other light, and, thus defended, it becomes an organ of inconceivable delicacy. Were water of uniform density perfectly free from suspended matter, it would, in my opinion, scatter no light at all. The track of a luminous beam could not be seen in such water. But an amount of impurity so infinitesimal as to be scarcely expressible in numbers, and the individual particles of which are so small as wholly to elude the microscope, may, when examined by the method alluded to, produce not only sensible, but striking, effects upon the eye.

"The results of the examination of nineteen bottles filled at various places between Gibraltar and Spithead are here tabulated.

"Here we have three specimens of water, described as green, a clearer green and bright green, taken in Gibraltar Harbour, and off Cabreta Point. The home examination showed the first to be thick with suspended matter, the second less thick, and the third still less thick. Thus the

green brightened as the suspended matter diminished in amount.

"Previous to the fourth observation our excellent navigating lieutenant, Mr. Brown, steered along the coast, thus avoiding the adverse current which sets in, through the Straits, from the Atlantic to the Mediterranean. He was at length forced to cross the boundary of the Atlantic current, which was defined with extraordinary sharpness. On the one side of it the water was a vivid green, on the other a deep blue. Standing at the bow of the ship, a bottle could be filled with blue water, while at the same moment a bottle cast from the stern could be filled with green water. Two bottles were secured, one on each side of this remarkable boundary. In the distance the Atlantic had the hue called ultra-marine; but looked fairly down upon it was of almost inky blackness—black qualified by a trace of indigo.

"What change does the home examination here reveal? In passing the indigo, the water became suddenly augmented in purity, the suspended matter becoming suddenly less. Off Tarifa, the deep indigo disappears, and the sea is undecided in colour. Accompanying this change, we have a rise in the quantity of suspended matter. Beyond Tarifa, we changed to cobalt-blue, the suspended matter falling at the same time in quantity. This water is distinctly purer than the green. We approach Cadiz, and at twenty miles from the city get into yellow-green water; this the London examination shows to be thick with suspended matter. The same is true at Cadiz Harbour, and also of a point fourteen miles from Cadiz in the homeward direction. Here there is a sudden change from yellow-green to a bright emerald-green, and accompanying the change a sudden fall in the quantity of suspended matter. Between Cape St. Mary and Cape St. Vincent the water changes to the deepest indigo, a further diminution of the suspended matter being the concomitant phenomenon.

"We now reach the remarkable group of rocks called the Burlings, and find the water between the shore and the rocks a strong green; the home examination shows it to be thick with fine matter. Fifteen or twenty miles beyond the Burlings we come again into indigo water, from which the suspended matter has in great part disappeared. Off Cape Finisterre, about the place where the *Captain* went down, the water becomes green, and the home examination pronounces it to be thicker. Then we enter the Bay of Biscay, where the indigo resumes its power, and where the home examination shows the greatly augmented purity of the water. A second specimen of water, taken from the Bay of Biscay, held in suspension fine particles of a peculiar kind; the size of them was such as to render the water richly iridescent. It showed itself green, blue, or salmon-coloured, according to the

direction of the line of vision. Finally, we come to our last two bottles, the one taken opposite St. Catherine's lighthouse, in the isle of Wight, the other at Spithead. The sea at both these places was green, and both specimens, as might be expected, were pronounced by the home examination to be thick with suspended matter.

"Two distinct series of observations are here referred to—the one consisting of direct observations of the colour of the sea, conducted during the voyage from Gibraltar to Portsmouth, the other carried out in the laboratory of the Royal Institution. And here it is to be noted that in the home examination I never knew what water was placed in my hands. The labels, with the names of the localities written upon them, had been tied up, all information regarding the source of the water being thus held back. The bottles were simply numbered, and not till all of them had been examined and described, were the labels opened, and the locality and sea-colour corresponding to the various specimens ascertained. The home observations, therefore, must have been perfectly unbiased, and they clearly establish the association of the green colour with fine suspended matter, and of the ultra-marine colour, and more especially of the black-indigo hue of the Atlantic, with the comparative absence of such matter.

"So much for mere observation; but what is the cause of the dark hue of the deep ocean? A preliminary remark or two will clear our way toward an explanation. Colour resides in white light, appearing when any constituent of the white light is withdrawn. The hue of a purple liquid, for example, is immediately accounted for by its action on a spectrum. It cuts out the yellow and green, and allows the red and blue to pass through. The blending of these two colours produce the purple. But while such a liquid attacks with special energy the yellow and green, it enfeeblens the whole spectrum. By increasing the thickness of the stratum we may absorb the whole of the light. The colour of a blue liquid is similarly accounted for. It first extinguishes the red; then, as the thickness augments, it attacks the orange, yellow, and green in succession; the blue alone finally remaining. But even it might be extinguished by a sufficient depth of the liquid.

"And now we are prepared for a brief, but tolerably complete, statement of that action of sea-water upon light to which it owes its darkness. The spectrum embraces three classes of rays—the thermal, the visual, and the chemical. These divisions overlap each other; the thermal rays are in part visual, the visual rays in part chemical, and *vice versa*. The vast body of thermal rays lies beyond the red, being invisible. These rays are attacked with exceeding energy by water. They are absorbed close to the surface of the sea, and are the great agents in evaporation. At the same time the whole spectrum suffers enfeeblement; water attacks all its rays, but with different degrees of energy. Of the visual rays, the red are first extinguished. As the solar beam plunges deeper into the sea, orange follows red, yellow follows orange, green follows yellow, and the various shades of blue, where the water is deep enough, follow green. Absolute extinction of the solar beam would be the consequence if the water were deep and uniform. If it contained no suspended matter, such water would be as black as ink. A reflected glimmer of ordinary light would reach us from its surface, as it would from the surface of actual ink; but no light, hence no colour, would reach us from the body of the water. In very clear and deep sea-water this condition is approximately fulfilled, and hence the extraordinary darkness of such water. The indigo, already referred to, is, I believe, to be ascribed in part to the suspended matter, which is never absent, even in the purest natural water; and in part to the slight reflection of the light from the limiting surfaces of strata of different densities. A modification of light is thus thrown back to the eye, before the depth necessary to absolute extinction has been attained. An effect precisely similar occurs under the moraines of glaciers. The ice here is exceptionally compact, and, owing to the absence of the internal scattering common in

bubbled ice, the light plunges into the mass, where it is extinguished, the perfectly clear ice presenting an appearance of pitchy blackness. (I learn from a correspondent that certain Welsh tarns, which are reputed bottomless, have this inky hue).

"The green colour of the sea has now to be accounted for; and here, again, let us fall back upon the sure basis of experiment. A strong white dinner-plate had a lead weight securely fastened to it. Fifty or sixty yards of strong hempen line were attached to the plate. My assistant, Thorgood, occupied a boat, fastened as usual to the davits of the *Urgent*, while I occupied a second boat nearer the stern of the ship. He cast the plate as a mariner heaves the lead, and by the time it reached me it had sunk a considerable depth in the water. In all cases the hue of this plate was green. Even when the sea was of the darkest indigo, the green was vivid and pronounced. I could notice the gradual deepening of the colour as the plate sank, but at its greatest depth, even in indigo water, the colour was still green. (In no case, of course, is the green pure, but a mixture of green and blue).

"Other observations confirmed this one. The *Urgent* is a screw steamer, and right over the blades of the screw was an orifice called the screw-well, through which one could look from the poop down upon the screw. The surface-glimmer, which so pesters the eye, was here in a great measure removed. Midway down, a plank crossed the screw-well from side to side; on this I placed myself and observed the action of the screw underneath. The eye was rendered sensitive by the moderation of the light; and, to remove still further all disturbing causes, Lieutenant Walton had a sail and tarpaulin thrown over the mouth of the well. Underneath this I perched myself on the plank and watched the screw. In an indigo sea the play of colour was indescribably beautiful, and the contrast between the water, which had the screw blades, and that which had the bottom of the ocean, as a background, was extraordinary. The one was of the most brilliant green, and the other of the deepest ultra-marine. The surface of the water above the screw-blade was always ruffled. Liquid lenses were thus formed, by which the light was withdrawn from some places and concentrated upon others, the water flashing with metallic lustre. The screw-blades in this case played the part of the dinner-plate in the former case, and there were other instances of a similar kind. The white bellies of porpoises showed the green hue, varying in intensity as the creatures swung to and fro between the surface and the deeper water. Foam, at a certain depth below the surface, was also green. In a rough sea the light which penetrated the summit of a wave sometimes reached the eye, a beautiful green cap being thus placed upon the wave, even in indigo water.

"But how is this colour to be connected with the suspended particles? Take the dinner-plate which showed so brilliant a green when thrown into indigo water. Suppose it to diminish in size, until it reaches an almost microscopic magnitude. It would still behave substantially as the larger plate, sending to the eye its modicum of green light. If the plate, instead of being a large coherent mass, were ground to powder sufficiently fine, and in this condition diffused through the clear sea-water, it would also send green to the eye. In fact, the suspended particles which the home examination reveals act in all essential particulars like the plate, or like the screw-blades, or like the foam, or like the bellies of the porpoises. Thus I think the greenness of the sea is physically connected with the matter which it holds in suspension. . . .

"At some distance below the Whirlpool Rapids we have the celebrated whirlpool itself. Here the river makes a sudden bend to the north-east, forming nearly a right angle with its previous direction. The water strikes the concave bank with great force, and scoops it incessantly away. A vast basin has been thus formed, in which the sweep of the river prolongs itself in gyrotory currents. Bodies and trees which have come over the falls are stated

to circulate here for days without finding the outlet. From various points of the cliffs above this is curiously bidden. The rush of the river into the whirlpool is obvious enough; and though you can imagine the outlet must be visible if one existed, you cannot find it. Turning, however, round the bend of the precipice to the north-east, the outlet comes to view.

To be continued).

CANADIAN MISSION IN LONDON.

It may be of interest to our readers to have some information as to the constitution and activities of the Canadian Mission, which has recently been established in London at 1, Regent Street, S.W. 1, by the Dominion Government.

The Mission was constituted by an Order of the Canadian Privy Council in November, 1918, and Mr. Lloyd Harris was appointed Chairman of the Mission. Mr. Harris is a Canadian business man who has a wide knowledge of the New Industrial Canada, which is one of the products of the Great War. He rendered invaluable service to the Dominion and to the Allied cause as head of the Canadian War Mission in Washington, and it was at the personal request of Sir Robert Borden, the Canadian Premier, that he consented to undertake his present duties.

The objects of the Mission are briefly:—

(a). The serious tonnage position arising out of the war coupled with the numerous restrictions put in force, both in the United Kingdom and in Canada, on import and export trade, tended to sever numerous old connections which had existed for generations between the Mother Country and the Dominion. It is one of the duties of the Mission to study the question at first-hand and to devise the means of re-establishing the traditional trade.

(b) A great work of reconstruction and re-organisation must be undertaken in Europe during the next few years in order to repair the devastating effects of the war. Raw materials, &c., will be necessary for this work, and many articles required can be obtained from Canada. The Mission hopes, by means of negotiations with the Governments of the countries concerned, to make arrangements for the supply of such goods to the advantage of all interests involved. It is further considering how by a system of credits to assist the Governments in purchasing the materials.

(c). The Mission is convinced that the resettlement of Europe is largely dependent on sufficient supplies of food being available and distribution being properly organised. The food can only be obtained in two ways:—(1) By imports from countries having margins for export; (2) By increased production in Europe itself.

Canada has large supplies which she is willing to place at the disposal of Europe, and, moreover, by reason of the fact that she has always specialised in the manufacture of agricultural machinery and implements, she is in a position to come to the assistance of the nations of Europe in their endeavours to produce supplies within their own borders.

In addition to foodstuffs of every description, Canada has available for export the following goods:—Paper and Paper Manufactures; Lumber; Wood Manufactures, including wood Pulp; Automobiles and other vehicles; Gasoline Launches; Drugs and medicinal chemicals; Leather and Leather Manufactures; Hides; Aluminium; Calcium Carbide; Asbestos; Iron and Steel Manufactures; Copper; Gold Quartz; Silver; Flaxseed; Nickel; Coal; Clothing; Furs; Agricultural Implements.

Canada seeks above all things to develop a larger interchange of trade with the Mother Country and, indeed, with all parts of the Empire. Canada has large markets

to offer British manufacturers, for she is a large buyer. Canada, too, feels that she can supply to this country many of the materials and manufactures which formerly were bought by Britain from the Central Powers.

The offices of the Mission are at 1, Regent Street, S.W. 1, and its personnel includes, besides Mr. Lloyd Harris, several other prominent Canadian business men who are well acquainted with the present industrial and economic position in Canada. They will at all times be willing to advise persons in the United Kingdom desirous of obtaining information with regard to Canadian Trade.

ORDERS OF THE MINISTRY OF MUNITIONS.

COPPER SULPHATE.

WITH reference to the Copper Sulphate Order, 1918, dated February 15, 1918, the Minister of Munitions hereby orders as follows:—

1. The operation of the said Order is hereby suspended on and after April 15, 1919, until further notice.

2. Such suspension shall not affect the previous operation of the said Order or the validity of any action taken thereunder, or the liability to any penalty or punishment in respect of any contravention or failure to comply with the said Order prior to such suspension or any proceeding or remedy in respect of such penalty or punishment.

3. This Order may be cited as the Copper Sulphate (Suspension) Order, 1919.

BLAST-FURNACE DUST.

In reference to the Blast-furnace Dust Order, 1917, dated August 7, 1917, the Minister of Munitions hereby orders as follows:—

1. The operation of the said Order is hereby suspended on and after April 30, 1919, until further notice.

2. Such suspension shall not affect the previous operation of the said Order, or the validity of any action taken thereunder, or the liability to any penalty or punishment in respect of any contravention or failure to comply with the said Order prior to such suspension, or any proceeding or remedy in respect of such penalty or punishment.

3. This Order may be cited as the Blast-furnace Dust (Suspension), Order, 1919.

GAS WORKS RETORT CARBON.

In reference to the Gas Works Retort Carbon, &c., Control Order, 1918, dated April 19, 1918, the Minister of Munitions hereby orders as follows:—

1. The operation of the said Order is hereby suspended on and after the date hereof until further notice.

2. Such suspension shall not affect the previous operation of the said Order or the validity of any action taken thereunder, or the liability to any penalty or punishment in respect of any contravention or failure to comply with the said Order prior to such suspension or any proceeding or remedy in respect of such penalty or punishment.

3. This Order may be cited as the Gas Works Retort Carbon, &c., Control (Suspension) Order, 1919.

NITRATE OF SODA.

The Minister of Munitions announces that the control of Nitrate of Soda will be suspended as on and from May 15, 1919. Transactions will be governed by the present licensing system until May 15, 1919. General licences will, however, be issued on application from now till May 15, 1919, authorising the holders of such licences to deal in Nitrate of Soda, but such licences will not authorise the holders to enter into any transaction which involves the actual movement of Nitrate except within the British Isles before May 15, 1919.

All applications for licences should be addressed to the Ministry of Munitions (Department of Explosives Supply), Storey's Gate, S.W. 1.

NOTICES OF BOOKS

The Applications of Electrolysis in Chemical Industry. By ARTHUR J. HALE, B.Sc., F.I.C. London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. 1918. Pp. ix+148. Price 7s. 6d. net.

THIS monograph gives a complete outline of the electrolytic methods used in chemical industry, which are continually increasing in number and importance. A short account is provided of the general principles of electrolysis, with definitions of the terms and units employed, and there is also a chapter on methods of generating the current, including primary and secondary cells and generators. Thus the student who knew practically nothing of electrical work could get a sufficient knowledge from the book to enable him to understand the subsequent chapters which deal with the applications of electrolysis firstly to the refining of metals. Full practical details of costs, &c., are supplied, and although some of these are unavoidably somewhat out of date they give some comparative indication of expenses and yields. The winning of metals is similarly discussed in detail, and a chapter is devoted to the electrolytic production of hydrogen and oxygen. The electrolysis of alkali chlorides is very fully treated, and some stress is laid upon the important developments of this industry which may be expected in the near future. In some cases processes which have been superseded are described if there are important lessons to be learnt from them, and the preparation of many miscellaneous inorganic and organic compounds is included.

Cast Iron in the Light of Recent Research. By WILLIAM HERBERT HATFIELD, D.Met. Second Edition, Revised and Enlarged. London: Charles Griffin and Co., Ltd. 1918. Pp. xvii+292. Price 12s. 6d. net.

AN excellent account of the equilibrium diagram of the iron carbide system is to be found in the early chapters of this well-known book, together with an admirable discussion of the influence of various factors upon the properties of cast iron. The author's accounts and criticisms of all the most important work which has been done in this region are exceedingly valuable, and no metallurgist can do without the book. A useful feature is the excellent appendix, which gives a full alphabetical list of names and terms used in metallurgical literature with both their French and German equivalents, and short explanations and definitions. The many illustrations and photomicrographs also add greatly to the value of the book. In the second edition much new matter has been added, including descriptions of the latest research work upon malleable cast iron. The report on the present position of the malleable castings industry in this country, which was prepared by the author at the request of the Committee of the Iron and Steel Institute for Foundry Practice, and approved by the Committee for presentation to the Ministry of Munitions, is reproduced in full. It is a most comprehensive and authoritative review of the industry, and is a valuable addition to the book.

I Fenomeni Elettro-Atomici sotto l'Azione del Magnetismo. ("Electro-atomic Phenomena under the Action of Magnetism.") By AUGUSTE RIGHI. Bologna: Nicola Zanichelli. Pp. xvi+435. Price 17.50 lire.

THE chief results of Prof. Righi's experimental work on the effect of a magnetic field upon the electric discharge are fully described in this treatise. An introductory chapter, which might perhaps be regarded as somewhat unnecessary, is provided for the general reader, and deals with elementary facts regarding the ether and electric phenomena, the electric discharge in rarefied gases, the ionisation of gases, &c. Then the effects of a magnetic field upon the

potential necessary to start the discharge are discussed, and a full account is given of the author's theory put forward to account for the observed facts. The study of luminous phenomena, and of the production of ionomagnetic rotations are treated in the following chapters. Many new and interesting facts are described, and an able exposition is given of the author's own theories, though the views of other workers are somewhat inadequately treated. The last chapter is devoted to the phenomena due to the action of a magnetic field upon currents in gases, in electrolytes, and in metals. The book is intended more particularly for readers who have made no special study of physics, and hence the use of mathematics is avoided as far as possible, although for those who wish to follow some of the necessary calculations they are discussed in a series of appendices.

Catalogue of Lewis's Medical and Scientific Circulating Library (including a Classified Index of Subjects, with the names of those authors who have treated upon them). New Edition revised to the end of 1917. London: H. K. Lewis and Co., Ltd., 136, Gower street, and 24, Gower Place, W.C. 1. Price 12s. 6d. net; to Subscribers 6s.

THIS extensive catalogue of books in Lewis's Circulating Library to the end of 1917 cannot fail to be useful. The Classified Index of Subjects is particularly valuable, as it enables one to see at a glance what works are available. It is very complete, occupying over a hundred pages.

NOTES.

ROYAL INSTITUTION.—Next Tuesday, April 29, at 3 o'clock, Prof. A. Keith will give the first of a Course of four Lectures on "British Ethnology—The People of Wales and Ireland." On Thursday, May 1, Dr. H. S. Hele-Shaw will give the first of two Lectures on "Clutches." The Friday Evening Discourse, on May 2, at 5.30 p.m., will be delivered by Prof. J. W. Nicholson on "Energy Distribution in Spectra"; on May 9, Sir George Macartney on "Chinese Turkestan—Past and Present." On Saturday, May 3, at 3 o'clock, Prof. H. S. Foxwell will give the first of two Lectures on "Chapters in the Psychology of Industry."

WE have received a copy of the "Directory of Paper Makers" for 1919, giving an alphabetical list of all the paper makers in England, Scotland, and Ireland, together with the names of paper makers' representatives, paper agents, &c. Much useful information on various subjects, such as watermarks, trade customs, sizes of papers, and paper trade publications, are given. The price of the catalogue is 2s. 6d. net post free in U.K., 2s. 9d. abroad.

IN the *Journal of the Board of Agriculture* for February, 1919, it is pointed out that on account of the extreme wetness of the winter months it will be necessary to apply nitrate or sulphate of ammonia to the crops to make up for the nitrates that have been washed out of the soil. In experiments with the wheat crop at Rothamsted last year it was found that the yield of grain in bushels per acre on undressed soil was 33'9; that produced where a dressing was given of superphosphates and sulphate of ammonia gave 41'3.

THE difficulty in obtaining tin-plate during the war has developed an important industry for the production of waterproofed cardboard. Containers for foodstuffs and other purposes that have hitherto been made from tin-plate are now made of cardboard rendered waterproof by impregnation with paraffin wax and other like materials, but the process most used is a varnish made from bakelite, an ammonia condensation product of carboic acid with

formalin, invented by Dr. L. H. Bakeland. The card vessels are coated with this material and stoved, and are thus found to be excellent substitutes for tin as well as being both lighter and cheaper. This manufacture will probably largely replace the familiar tin can.

MR. WILLIAM RUDDERHAM, for many years general manager, and since 1915 a director of Coleman and Co., Ltd., Norwich, has been appointed managing director in place of the late Mr. W. C. Snelling.

At the Extraordinary General Meeting of the Chemical Society on May 8 the following resolutions will be proposed:—(1) That women should be admitted to the Society on the same terms as men. (2) That in the election of Officers and Council a postal vote of Fellows resident in the United Kingdom should be taken. (3) That every alteration of the by-laws should require for its adoption a two-thirds majority of those voting. (4) That no alteration of the by-laws should become effective until one month after its adoption has elapsed, within which period it should be competent for not less than thirty Fellows to demand a poll of all Fellows resident in the United Kingdom. (5) That the number of ordinary members of Council should be raised to at least eighteen. (6) That the class of "Associates" should be abolished. (7) That the term "Honorary and Foreign Members" should be replaced by "Honorary Fellows." (8) That the limit placed by the Charter on the yearly value of the Society's premises should be raised. In the event of any or all of the foregoing resolutions being adopted, the following further resolution will be moved:—(9) That the Council be and hereby is empowered to take steps to secure a Supplementary Charter giving the necessary power to alter the by-laws in the sense of the foregoing resolutions.

MR. W. S. BARCLAY, of the Federation of British Industries, sailed on Saturday last for South America to act as a Special Commissioner to conduct back to this country the Brazilian Delegates who have been appointed by the Brazilian Government to undertake a tour to this country as the guests of the Federation. Mr. Barclay was attached to the recent Mission to Brazil under Sir Maurice Bunsen, and has therefore had exceptional opportunities of appreciating the problems of Anglo-Brazilian Trade. At the end of the present tour of these Brazilian Delegates the Federation intends to send a permanent Commissioner to Brazil as part of its Overseas Commissioner Service. It will be remembered that the Federation, last autumn, entertained a number of Greek Delegates under the leadership of the Greek Minister of Agriculture and conducted them over many of the largest manufactories in this country. As an outcome of this tour the Federation has arranged a British Industrial Exhibition at Athens in the near future which should prove most beneficial to British Manufacturers. The Federation intends to continue this policy of bringing delegates from abroad to this country and thus fostering in every way friendly relations between British manufacturers and potential customers from all over the world.

THE SWISS TRADES Exhibition will be held at Basle from April 24 until May 8. This Exhibition was first held at Basle in April, 1917, when the exhibitors numbered 831. In 1918 they increased to 990, and at the third exhibition this month there will be 1300 firms showing their products. In 1917 business to the amount of 20 to 25 million francs was done; last year that amount was doubled. Between two and three hundred thousand visitors attended the first and second exhibitions, and the number of buyers last year was 18,000. It is claimed that the Swiss Trade Exhibition in Basle is not a copy of any foreign exhibition; it enjoys in its present organisation and development a special Swiss character. It aims not only at an increase of the Swiss home trade, but also at an extending of the Swiss exports. The goods offered are purely Swiss, and a strict control is stated to exclude all foreign products

from participation in the Swiss Trade Exhibition. The general public are admitted two days in the week, according to the principle: "The Exhibition is a means of communication to connect buyers and exhibitors." The goods offered are divided into the following nineteen groups:—Articles of food and luxuries; Drugs and Chemicals; House and Kitchen utensils, Household goods, Glass and China; Fittings for apartments, Furniture and Basket goods; Heating, Light, and Sanitary fittings; Technical articles in metal, wood, glass, cork, leather, india-rubber, &c.; Office and Shop fittings, Office articles, Drawing and Painting utensils; Paper manufactures and Graphic arts; Musical instruments and Music; Articles of sport and toys; Artistic industrial articles; Clocks, Watches, and Jewellery; Textile Goods, Clothing and Outfitting (boots, leather and celluloid articles, fancy goods, drapery); Machinery and Tools; Fine mechanical instruments, Instrumenta and Apparatus; Electrical industry; Raw materials and Building materials; Agriculture and Horticulture; Sundries. For the Exhibition of 1919 twice as much ground as last year is required. All buyers, after sending in a written notification for the visit, receive a buyer's card with their name, which is available for two days, but can be renewed if necessary. The buyers' cards are only issued for those genuinely interested. The list of the buyers was closed on April 5, 1919. Prospective visitors who hold credentials from a British Authority, or their Chamber of Commerce, can receive all necessary information by addressing M. Henri Marten, First Secretary of Legation and Commercial Adviser, the Swiss Legation, 32, Queen Anne Street, Cavendish Square, London, W. 1.

IRON AND STEEL INSTITUTE.—*Annual Meeting, 1919.*—The Annual Meeting of the Institute will be held, by kind permission, in the House of the Institution of Civil Engineers, Great George Street, Westminster, on Thursday and Friday, May 8 and 9, 1919, commencing on Thursday at 10.30 a.m., and on Friday at 10 a.m. The following is the programme of the proceedings:—

Thursday, May 8 (at 10.30 a.m.).

General Meeting of Members.

The Council will present their Report for the year 1918. The Hon. Treasurer will present the Statement of Accounts for 1918.

Scrutineers will be appointed for the examination of voting papers for the election of new Members and Associates of the Institute.

Award of the Bessemer Medal for 1919 to Prof. Cav. Federico Giolitti, Ph.D. of Turin.

Papers Nos. 6, 8, 3, 16, 17, will be read and discussed.

The Meeting will be adjourned.

Joint Session (by invitation of the Institution of Electrical Engineers) to discuss papers on Electric Steel Furnaces. The following is a list of the papers likely to be submitted:—

"Developments in Iron and Steel Electric Furnaces," by J. Bibby; "The Booth Hall Electric Furnace," by W. K. Booth; "The Development of the Electric Melting Furnace," by D. F. Campbell; "The Control of Electric Arc Furnaces," by H. Coates; New Type of Electric Furnace," by Axel Sahlin; "Large Electric Furnaces," by Victor Stobie.

Members who desire to take part in the discussion can obtain copies in advance on application to the Iron and Steel Institute.

Friday, May 9 (at 10 a.m.).

General Meeting of Members.

The award of grants from the Andrew Carnegie Research Fund in aid of research work will be announced.

Papers Nos. 11, 10, 1, 2, will be read and discussed.

Afternoon Session to read and discuss papers 15, 7, and 12.

Those papers for which time cannot be found will be taken as read and discussed by correspondence.

The following is a list of Papers that are expected to be submitted:—

1. J. H. Andrew: "Manufacture and Working of High-Speed Steel."
2. J. O. Arnold and F. Ibbotson: "Molecular Constitutions of High-Speed Tool Steels and their Correlation with Lathe Efficiencies."
3. C. H. F. Bagley: "Modern Steel Metallurgy."
4. G. Cearo: "Note on the Liquidus in the Iron-Carbon Diagram."
5. G. Watson Gray: "Estimation of Phosphorus in the presence of Tungsten."
6. L. Greiner: "Report on the Condition of Belgian Iron and Steel Work after the German occupation."
7. D. Hanson and J. E. Hurst: "Improvements in the Case-Hardening Process."
8. L. C. Harvey: "Use of Powdered Coal."
9. K. Honda: "On the Non-Allotropic Nature of the α_2 Transformation in Iron."
10. J. C. W. Humphrey: "Macro Etching and Printing."
11. H. M. Howe: "A Review of Work of United States National Research Council."
12. A. McCance: "Carburisation of Iron at Low Temperatures."
13. A. M. Portevin and M. Garvin: "An Experimental Investigation of the Influence of the Rate of Cooling on the Hardening of Carbon Steels."
14. K. Tawara and G. Asahara: "On Graphitisation in Iron-Carbon Alloys."
15. G. Taylor: "Some Points in the Manufacture of Files."
16. J. H. Whiteley and A. F. Hallimond: "The Acid Hearth and Slag."
17. B. Yaneske: "Deoxidation, and the Influence of Lime on Equilibrium in the Acid Open-Hearth Furnace."

NOTES FROM FOREIGN SOURCES

Margarines and their Richness in Butter.—M. W. Arnold.—When margarines were made only of fats and oils possessing a fairly low Reichert-Meissl index it was comparatively easy to deduce the proportion of butter they contained from the index. Now, however, when coco butter and palm nut oil are so largely used for making margarine it has become a much more difficult task. In order to obtain definite information as to the presence of butter in margarine it is necessary to determine—(a) the index of saponification, (b) the Reichert-Meissl index, (c) the Polenske index (of the original fats and the fats treated with alcohol), and (d) the molecular weight of the water-soluble fatty acids. Margarine can then be classed as follows:—(i.). Those containing neither butter nor palm oil. If both the Reichert-Meissl index and the Polenske index of the original fats do not exceed 0.55 neither butter nor palm oil can be present. (ii.) Those containing butter. The absence of palm oil is shown by a low Polenske index, while the presence of butter may be deduced from the high Reichert-Meissl index. The molecular weight of the water-soluble fatty acids lies between 97 and 107 (benzoic acid, which increases the Reichert-Meissl index has a molecular weight of 122). (iii.). Those containing coco-butter. The presence of palm oil is indicated by a Polenske index above 0.6 and molecular weights of the soluble fatty acids between 130 and 144. To decide whether coco-butter or palm oil is present it is important to take into account the relation existing between the Reichert-Meissl and Polenske indices. If a little of both is present the physical state of the Polenske acids must be taken into account. (iv.). Those probably containing palm oil. In this case the Polenske index is

above 0.6, the molecular weight of the water-soluble acids is between 130 and 136, and the Polenske acids are, if the percentage of palm oil is pretty high, generally solid or semi-fluid, and not clear. (v.). Those containing butter and coco butter. The Polenske index is higher than 0.55, and often higher than 0.6. The Reichert-Meissl index is relatively higher than in the case of the absence of butter, and the molecular weight of the acids lies between 110 and 130. (vi.). Those containing butter and palm oil. These are characterised by the fact that the Polenske acids are solid, and by the fact that the Polenske index of the fats treated with alcohol is only 2.0.—*Zeitschrift für Untersuchung der Nahrungs und Genussmittel*, xxvii., 379.

New Reagent for Bases and Acids.—Marc Chavivier.—A decoction of red beetroot is an excellent reagent for bases and acids. It may be prepared by simply boiling pieces of beetroot in water and filtering, when a reddish violet very opalescent liquid is obtained. A drop of potash turns it dark yellow, while mineral acids and even the weakest organic acids turn it back to its original colour. The reagent is very sensitive, a solution of 1 gm. of boric acid in a litre of water reddening it very decidedly, after it had been decolorised by lime. The reagent cannot be used in the form of paper, as it is not readily fixed on paper. It does not appear to be a true solution but a colloidal hydrosol.—*Bull. Soc. Chim. de France*, 1919, xxv.-xxvi., 118.

Diffusion of Light by Molecules of Air.—J. Cabannes.—In 1914 the author undertook an experimental study of the diffusion of light by molecules of gas, and showed that it was possible to observe light diffused by some cc. of air, freed from dust, in normal conditions of temperature and pressure. These researches, which were confirmed by Strutt, were interrupted by the war. Wood has recently thrown doubt upon these results, and suggests that the observed diffusion might be due to mist produced in the air by ultra-violet radiations. The author now points out the precautions that must be taken in order to do away with disturbing phenomena. It is clear that certain ultra-violet radiations may introduce complications in the study of light diffused by gases, and in order to verify Lord Rayleigh's theory experimentally it is best to exclude radiations of wave-length below 0.3μ . By a photographic method, however, it is possible to study the diffusion of radiations of high frequency by molecules of air. It is necessary to illuminate only a small part of the gaseous mass contained in a closed vessel, and that only for very short periods (ten to thirty seconds) separated by fairly long intervals (ten to thirty minutes).—*Comptes Rendus*, 1919, clxviii., 340.

Influence of Light upon the Absorption of the Organic Matter of the Soil by Plants.—Dolorès Celian de Besteiro and M. Michel-Durand.—In 1911 Cailletet pointed out that certain plants live normally in light which appears to be too faint to enable them to assimilate carbon dioxide sufficiently from the air, and he suggested that these plants, being unable to obtain all the carbon they require from the air, might derive a considerable amount from the soil in the form of organic matter. The authors have taken up the question, experimenting for the purpose with a plant which is a heliophyte, viz., *Pisum sativum*. They grew the plants in a culture consisting of Knop's liquid, containing 4 parts per thousand of glucose, and exposed them to varying intensities of illumination. From determinations of the increase of dry weight of the plants, the glucose absorbed by each plant, the glucose absorbed per gm. of dry weight of the root, and that absorbed per gm. of dry weight of the entire plant the following conclusions could be drawn:—(i.). The plants increased more in weight the more intense the illumination to which they were exposed. (ii.). The roots also were better developed in stronger illuminations. (iii.). The plants which grew in a more intense light absorbed more glucose. (iv.). The same weight of root absorbed decidedly more glucose in faint than in strong lights. (v.). The same

weight of whole plant absorbed practically the same amount of glucose in illuminations of different intensities. This last conclusion shows that the plant is incapable of augmenting the absorbing power of its roots so that they can extract more organic carbon from the soil. Thus there is neither parallelism nor compensation between the absorption of carbon by the green leaves in the carbon dioxide of the air and the absorption of organic carbon from the soil by the roots.—*Comptes Rendus*, 1919, clxviii., 467.

Discovery of a New Glucoside "Loroglossine."—Em. Bourquelot and M. Bridel.—The authors have applied the biochemical method of investigation to various indigenous kinds of orchids, e.g., *loroglossum*, *orchis*, *ophrys*, &c. In one of these (*L. hircinum*) they have discovered a new glucoside, to which they have given the name "Loroglossine." The aqueous extract of the plant was exposed successively to the action of invertine (reagent for cane sugar) and emulsine (reagent for glucosides). They found that the plant, like all phanerogams, contains cane sugar. It also contains a glucoside hydrolysable by emulsine and a fairly large proportion of a dextrogyratory principle, which is not attacked by ferments, for after the action of the invertine the liquid is still dextrorotatory, while the glucoside not yet hydrolysed is levorotatory. Loroglossine crystallises in long colourless needles; it is odourless and very bitter; very soluble in water and alcohol, very slightly soluble in acetic ether and acetone. It is levorotatory, does not reduce cupric liquid, and is hydrolysed by warm dilute sulphuric acid, as well as by emulsine.—*Comptes Rendus*, 1919, clxviii., 701.

Researches on Chemical Luminescence.—J. Lifschitz.—The study of the emission of light in chemical reactions, like that of the absorption and chemical effects of light, may lead to important results concerning the connection between radiant and chemical energy and the nature of chemical forces. The phenomenon of chemical luminescence has been observed in many reactions, and not by any means in oxidation processes only. For example, a beautiful luminescence appears when hydrobenzamide is distilled in a current of hydrogen, lophin being the product, while various decompositions of unknown nature occur simultaneously. Thus the reaction is essentially an intramolecular transposition. Other reactions show that the appearance of chemical luminescence is not dependent either upon the total amount of energy transformed or upon the velocity of the reaction. For instance, nitrogen dioxide acts at least as energetically upon phenyl magnesium bromide as air, but it is only with the latter that chemical luminescence is observed, and then only in absence of moisture. It has been shown that when ethereal Grignard's solutions react with oxygen chemical luminescence appears in the case of aromatic organo-metallic compounds, but not with aliphatic compounds, this difference being due to the different stability of their etherates. The same phenomenon is observed with the addition products of organo-magnesium compounds with dimethyl aniline. The total liberation of heat in the formation of etherates seems to be less with the aromatic Grignard compounds than with the aliphatic compounds.—*Helvetica Chimica Acta*, 1918, i., 472.

MEETINGS FOR THE WEEK.

TUESDAY, 29th.—Royal Institution, 3. "British Ethnology—The People of Wales and Ireland," by Prof. A. Keith.

THURSDAY, May 1st.—Royal Institution, 3. "Clutches," by Dr. H. S. Helle Shaw.

— Royal Institution, 5. (Annual Meeting).
— Institution of Electrical Engineers, 6. "Magnetic Stermia," by Dr. C. Chree.

FRIDAY, 2nd.—Royal Institution, 5.30. "Energy Distribution in Spectra," by Prof. J. W. Nicholson.

SATURDAY, 3rd.—Royal Institution, 3. "Chapters in the Psychology of Industry," by Prof. H. S. Foxwell.

Assayer, aged about 25, with knowledge of Gold and Silver Assaying, required at once. Permanent position; good prospects; Birmingham. State age, experience, and salary required.—Address, "A. 25," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Assistant Chemist desires Position in a Laboratory. Has had two years' experience in Acid Analyses, and also two years' Inorganic Chemistry and Qualitative Analyses in College. Would commence at moderate salary.—Address, Mr. J. Parkes, 13, Clarence Road, Ponders End, Middlesex.

CHEMIST.—Wanted for Factory Testing work, qualified Analytical Chemist.—Apply, giving full particulars, to Manager, The Imperial Tobacco Co., Ltd., Dingley Road, City Road, E.C. 1.

Discharged Soldier desires Situation in Chemical Laboratory. Specially qualified in Metallurgical Analysis of Rare Metals.—Address, D. S., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Enterprising Assistant Chemist (21) desires a Position in a Laboratory or Works. Formerly Assistant Chemist, Directorate of Chemical Inspection, and capable of undertaking any Inorganic Analyses. Would commence at moderate salary.—Address, Mr. W. G. Richards, 7, Sivell Place, Heavitree, Exeter.

Junior Chemist (20), Inter. B.Sc. (Lond.), previous experience, seeks Situation in London Laboratory or Works.—Address, L. L., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Laboratory Attendant, having a fair knowledge of General Chemistry and good experience, wanted. State wages required and full particulars.—Address, "Investigator," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Two Analytical Chemists are required for a large Testing Laboratory. Commencing salary £200 per annum. It is desired that applicants should have had at least two years' experience in the Laboratories of Steel or other Metallurgical Works. Preference given to those who have fought in the War.—Address, "Analytical," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

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THE CHEMICAL NEWS

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THE ANALYSIS OF SAUSAGES, MEAT PASTES, AND ARMY RATIONS.

By A. W. STOKES, F.I.C.

Sausages.—While the "Food Control Regulations" lay down qualities and prices for sausages, requiring that the meat should be, for one price, 50 per cent and, for another price, 67 per cent by weight, it is necessary to be able to determine these limitations. Having analysed over 60 samples a description of the method I have used may be of interest.

The main constituents of sausages are meat, bread, and water. A little salt and spice are usually added. Whilst the meat may be derived from any part of the animal it is, of course, in most cases impossible to determine either the animal or the part used.

The water is the chief difficulty. In the following analyses of all meat products I have assumed that meat naturally contains 70 per cent and bread 40 per cent of water. The meat is dissolved by boiling in alcoholic soda solution, with formation of a soap from the fat. The insoluble matter is then placed in an aqueous caustic soda solution to dissolve the starch, which is then precipitated by strong alcohol.

The actual method used is as follows:—The total solids, water, and ash are estimated in the usual way on 5 grms. of the material. Boric acid may be looked for in the ash. Ten grms. are boiled for one hour in alcoholic (methylated) solution of caustic soda (the alcohol being of at least 90 per cent, and the caustic soda of 5 per cent strength) under a reflux condenser. This treatment should dissolve the meat, form a soap with the fat, and leave the starch unaltered. This is filtered while hot through a small plug of slag-wool, and washed with strong hot alcohol. The filtrate is cooled and made up to 250 cc. with water, and 25 cc. evaporated to about 15 cc. (to remove the alcohol). The fatty acid is determined in this, using the Schmid method as in milk analysis. The filter-plug and residue are returned to the original flask; about 100 cc. of cold aqueous 5 per cent soda solution are added and left for one hour, with occasional shaking. This will dissolve the starch. The volume is made up to 500 cc. with cold water and filtered through a small slag-wool plug. Fifty cc. are collected, and about 100 cc. of strong alcohol (90 per cent) are added to precipitate the starch; after stirring and allowing to stand for half-an-hour the starch is filtered through counterpoised filter-papers, washed with alcohol, dried, and weighed. The filtrations are sometimes difficult, but may easily be managed without a filter-pump if a filter-flask be used to which is attached a short piece of rubber tube; mouth suction is applied to the end, the tube doubled over, and a clip applied to the part doubled.

Calculation.—The fatty acids may be assumed to equal 95 per cent of actual fat. From the total solids are subtracted the starch and fat to get, by difference, the dry meat. To this "dry meat" is added 2.33 times its weight of water; this will give the fat-free flesh (called "flesh" in the following tables). To the starch is added 0.66 times its weight of water to form bread.

Frequently it will be found that the water actually present is above the quantities allowed by this calculation. This is due to the fact that in the manufacture of sausages the crusts and the bread used are soaked in water to soften them, and this water is only partially squeezed out before being chopped up with the meat. Very rarely the bread or the meat may contain less than the amounts I have

allowed for water. The ash consists mainly of salt, though in 12 out of 60 samples analysed boric acid was also present, but in small amounts. The total ash varied from 1.2 to 3 per cent, with an average of 2 per cent.

The results obtained from the five following samples may be of interest; they are selected (Table I.) as showing mainly the extremes of each ingredient.

TABLE I.—Sausages.

Per cent.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	Average of 60 samples.
Fat	0.9	20.2	9.5	6.9	20.9	11.2
Bread	9.5	16.7	5.3	32.2	29.4	20.3
Flesh	89.1	72.2	71.0	51.1	26.0	60.2
Water present	66.8	48.1	66.0	58.4	53.6	58.6
Water allowed	66.3	57.2	51.8	48.6	29.9	50.3
Water excess..	0.5	—	14.2	9.8	23.7	8.3

The smallest amount of water found to be present was 48 per cent (No. 2); this sample it will be observed sums up to 109.1 per cent. This and three other samples were the only specimens showing that the meat and the bread contain less than the calculated allowances of water. No. 5, which contained the largest excess of water (23.7 per cent), was seen by microscopical examination to consist largely of tripe.

In only a few cases were these samples examined microscopically; usually the indications were not particularly useful. Some few were analysed before and after cooking; generally the amounts of water and of fat diminished after cooking. But, as no standard for water could be assumed for these, the results are of little interest, and are not recorded here.

Meat Pastes. Meat pastes, variously described as ham and chicken, tongue and chicken, veal and ham, ham and tongue, ham, tongue, and chicken, turkey and tongue, and wild duck, prepared by various makers, were analysed in the same way. The results of 14 of these show for the extreme percentages of each of the ingredients (Nos. 1 to 5), and the averages for all are given in Table II.

TABLE II.

Per cent.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	Average of 14 samples.
Fat	3.6	16.6	15.4	13.4	11.1	13.2
Bread	11.0	3.0	6.7	13.8	13.6	8.7
Flesh	61.0	85.3	63.2	45.1	41.1	63.6
Water present	71.6	55.9	61.6	65.0	69.0	62.6
Water allowed	47.0	60.9	46.9	37.3	34.2	48.1
Water excess..	24.6	—	14.7	27.7	34.8	14.5

The only sample out of these 14 that summed up to over 100 was No. 2, which, on the allowances for water in the flesh and bread, totalled to 104.9 per cent. This was in every respect far above all the other samples, containing the least amount of bread and no excess of water. On reference to the maker I was informed that my results were within 2 per cent of the materials used.

Of the samples the highest ash was 5.28 per cent, but this was mainly due to common salt; the lowest was 1.48, the average 2.9 per cent. No boric acid was present in any of these.

To see how the process would work in various hands Messrs. G. A. Stokes and E. W. Wright kindly analysed a few samples of sausages for me. Their results were very similar to mine, as shown by the example Table III.

TABLE III.

Per cent.	G. A. S. and E. W. W.	A. W. S.
Fat	14.5	14.2
Bread	28.0	27.8
Flesh	39.5	41.0
Water excess ..	18.0	17.0

Army Rations.—A number of army rations were examined to see if they complied with the contract

specifying them to contain not more than 12 per cent fat, or 170 per cent water, or more than 2 grains of tin per pound. They were not to have a greater acidity than the equivalent of 72 cc. of N/10 soda in 100 parts. They consisted of mixtures of meat, potato, haricot beans, peas, carrots, and onions cooked in sealed tins.

It was found easiest to pick out all the meat separately and to shred this finely. The vegetables could readily be mashed and mixed in the tin, the meat then added, and the whole well incorporated in the same tin so as to absorb any moisture therein. The analyses of these were performed as in the case of the sausages, omitting, however, assay estimation of starch.

For the acidity, 5 grms. were shaken with 100 cc. of cold water for one hour; an aliquot part was then titrated, after filtration, with N/10 soda. The results of 5 samples are appended (Table IV.).

TABLE IV.

PER CENT.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	Average.
Fat	11.7	4.9	8.2	8.2	8.1	8.2
Water	67.5	73.0	67.4	68.0	68.4	68.8
Acidity	16.0	32.0	48.0	32.0	30.0	31.6
Ash	1.2	1.3	1.4	1.3	1.6	1.4

Only in one case (No. 2) was the amount of water slightly beyond the limit. In no case was any tin or boric acid detected.

A review of the results of the analyses of the sausages and meat pastes shows that an excess of water, not natural to the meat and bread, may in the sausages reach about 24 per cent, and in the meat pastes 35 per cent. This high excess is usually due to the use of much bread; this soaked in water enables a large amount to be incorporated.

In the United States the use of any starchy matter in sausage is forbidden. It is to be regretted that such is not the case in England. A sample like sausage No. 5, which contains about equal parts of fat (21 per cent), meat (26 per cent), bread (29 per cent), and excess water (24 per cent), would not be possible were it illegal to use bread.

I am greatly indebted to Mr. G. W. Bender for his assistance in this work.

DISCUSSION.

The PRESIDENT, in opening the discussion, said that the Ministry of Food had consulted the Society in reference to the carrying out of their Sausage Orders under the following circumstances:—On January 21, 1918, the Department found it necessary to introduce the meatless days, and in that Order, known as the Public Meals Order, the expression "meat" was deemed to include sausages. In February the Meat Licensing Order was issued which forbade any person after March 15 from dealing in dead meat without a licence, and in this Order sausages were included as dead meat. This was revoked in Ireland on June 17, but later in the year the Ministry again issued an Order in which they then fixed the price of sausages according to their meat content, ignoring the fact that sausages were supposed by the previous regulations to be all meat. Pork sausages had also not been included in their Pig and Pig Products (Prohibition of Export) Order, as only bacon, ham, and lard were included in it. The Government Laboratory had tried to solve the mystery of what is now meant by a sausage of different grades, and the Society was glad to welcome their contribution to the discussion.

Dr. VORLOKER suggested that it would be better if the Ministry of Food and other Government Departments, before making their Orders and putting out regulations as to how mixed foods should be compounded, would consult analysts generally and the Government Laboratory in particular as to whether it was possible to ascertain by analysis whether the composition could be ascertained, and not wait, as was here done in the instance of sausages, &c., to hear the difficulties expressed at a subsequent meeting of this Society.

It seemed to him that the authors of the papers they had heard read relied mainly upon the amount of nitrogen shown in the analysis, and reckoned this as representing the meat present. He would like to ask what would happen if he sprinkled a little sulphate of ammonia over a sausage or mixed some leather powder with it—would this be reckoned as "meat"?

He had heard no mention of microscopical analysis in this connection, and thought that it should be employed. The inclusion of soya bean meal, for instance, could be so detected.

Mr. CRIBB inquired if the Food Controller had drawn up any definition of "meat," as the value of the methods proposed in the two papers under discussion must largely depend on what was meant by that word.

In pre-war days he had had occasion to examine some sausages which consisted almost entirely of fat and bread, with a little connective tissue and only a trace of muscle fibre. Would such a mixture comply with the "Order"?

An ingenious manufacturer might put a large proportion of gristle and connective tissue into his sausage meat. This, owing to the low nitrogen factor for gelatin as compared with that for proteins, would seriously affect the figure for "flesh" obtained by the method recommended by Messrs. Stubbs and More. The presence of anything like a substantial proportion of liver, owing to the glycogen present, would give trouble in other directions.

In view of these difficulties he would like to see a number of analyses, by the methods now put forward, of sausages of known composition, as by this means only would it be possible to decide whether the problem set by the Ministry of Food could be satisfactorily solved. In any case he thought that the analytical figures obtained would have to be interpreted with great caution, and it would be quite unsafe to take action in cases anywhere near the border-line.

With regard to sausage skins, to which the President had referred, some years ago he was consulted about a large consignment of sausages which on being sent to America were refused admission to that country, on the ground that they contained boric acid. The manufacturers had put in none, and he was quite unable to find any in the sausages as a whole; but it transpired that the authorities in America had actually examined the skins separately, and had found an extremely minute trace of boric acid, which on examining a number of the skins he afterwards ascertained to be between one and two parts per million.

The skins before use were kept in a saturated salt solution, and this was the only apparent source from which the boric acid could have been derived. Skins kept in this way would presumably be sterile.—*The Analyst*, xlv., No. 517, p. 127.

PHYSICAL CHEMISTRY AND ITS BEARING ON THE CHEMICAL AND ALLIED INDUSTRIES.*

By Prof. JAMES C. PHILIP, O.B.E., M.A., Ph.D., D.Sc.

(Continued from p. 197).

THE systematic study of homogeneous catalysis has led to very definite and interesting results, some of which may be illustrated by a couple of examples. The first of these refers to the influence of the concentration of the catalyst, and is based on a study of the rate at which diazoaminobenzene is converted into aminoazobenzene. This change takes place in aniline solution when an aniline salt, acting as catalyst, is present. The course of the reaction can be followed quantitatively, and the rate of change is expressible by a velocity coefficient, the value of which varies in

* Cantor Lecture (11.). Delivered before the Royal Society of Arts, December 9, 1918. From the *Proceedings of the Royal Society of Arts* [xvii.], No. 3451.

direct proportion to the concentration of the catalyst, other conditions being unaltered. This is apparent from the figures given in Table IV.

TABLE IV.—*Diazoaminobenzene* $\rightleftharpoons$ *Aminoazobenzene*.

Concentration of aniline hydrochloride.	Velocity coefficient at 35°.
0.1	0.0060
0.2	0.0123
0.3	0.0180

Again, in cases of homogeneous catalysis it is possible to compare the efficiency of different catalysts under given conditions. The change of cane-sugar, for example, into invert sugar takes place with appreciable rapidity in presence of an acid as catalytic agent, and can easily be followed with a polarimeter. The course of the reaction is in harmony with the formula for a unimolecular reaction ; i.e., the velocity coefficient $k = \frac{1}{t} \cdot \log_e \frac{a}{a-x}$.

This will be seen in Table V.

TABLE V.—*Inversion of Cane sugar by N/2 HCl at 25°.*

t minutes.	Angle of rotation.	$\frac{1}{t} \log_e \frac{a}{a-x}$.
0	+25.16°	—
56	16.95°	0.00501
116	10.38°	0.00501
176	5.46°	0.00504
236	1.85°	0.00504
371	-3.28°	0.00508
∞	-8.38°	—

Now it is found that the rate of inversion of cane-sugar at a given temperature in presence of acid of a definite normality varies notably with the nature of the acid. Thus the catalytic efficiency of hydrochloric acid in promoting the inversion of sugar is greater than that of sulphuric acid and acetic acid at the same temperature and the same concentration, and, indeed, for N/2 concentration, the velocity coefficients obtained in the three cases stand in the ratio 100:54:0.4. So far, then, as homogeneous catalysis is concerned, the evaluation of velocity coefficients provides a rational method of comparing the activity of different catalysts under the same conditions.

The majority of the technically important catalytic reactions belong, however, to the "heterogeneous" class, and in these cases the application of the reaction velocity formula already discussed and illustrated cannot be carried through to anything like the same extent. Indeed, the careful study of cases of heterogeneous catalysis on quantitative lines reveals the fact that other factors are operative besides mass action. This is brought out very clearly, for example, by Bone and Wheeler's research on the combination of hydrogen and oxygen at hot surfaces.

In this work provision was made for the circulation of hydrogen and oxygen through a tube packed with fragments of unglazed porcelain and maintained at a constant temperature, the gradual combination of the gases which took place under these conditions being followed quantitatively by determinations of the pressure from time to time. Plainly, as the reaction $2H_2 + O_2 = 2H_2O$ proceeds, the pressure falls regularly, and provides a record of the progress of the change. From such a record the velocity of combination of the gases may be calculated.

On the ground that two distinct substances disappear during this reaction it might fairly be expected that the course of the change would conform to the bimolecular or the trimolecular type. The surprising result, however, has emerged that the rate of reaction is represented by the unimolecular formula. In support of this the figures in Table VI., obtained with normal electrolytic gas at 450°, may be quoted:— k_1 is the velocity coefficient calculated by the unimolecular formula, k_2 is that based on the bimolecular formula.

TABLE VI.

t hours.	Pressure in mm.	k_1 .	$k_2 \times 10^6$.
0	465.6	—	—
12	324.0	0.0131	78.2
24	228.6	0.0129	92.8
36	163.9	0.0126	109.8
48	116.1	0.0125	134.7
72	60.7	0.0123	199.0
96	28.6	0.0126	341.8
120	14.6	0.0125	552.7

Experiments were made also in which the initial mixture contained hydrogen and oxygen in other than the volume ratio 2:1, and in which the partial pressures of the separate gases were ascertained at each stage, as well as the total pressure. A unimolecular constant w was then calculated for the rate of disappearance of each gas separately, viz., k_{H_2} and k_{O_2} , and it was found that the former alone was constant. This important result may be illustrated by the figures obtained with a mixture of 3 volumes of hydrogen with 1 volume of oxygen, circulated over porcelain at 430°. The quantities P_{H_2} and P_{O_2} are the partial pressures of hydrogen and oxygen at the successive stages (Table VII.).

TABLE VII.

t hours.	P_{H_2} mm.	P_{O_2} mm.	k_{H_2} .	k_{O_2} .
0	292.5	94.9	—	—
2	260.5	78.9	0.0253	0.0401
4	230.5	63.9	0.0259	0.0429
6	206.2	51.8	0.0253	0.0438
8	185.9	41.7	0.0241	0.0447
12	151.8	24.6	0.0237	0.0488
16	123.6	10.4	0.0240	0.0600

From these and other figures it appears that the rate of change is proportional to the partial pressure of the hydrogen, and this must mean, as Bone has pointed out, that the formation of steam is an indirect process, dependent on a primary change, at the surface of the catalyst, in which hydrogen is concerned. The evidence favours the view that the catalytic action of porcelain depends on the occlusion of the reacting gases on its surface, and the results quoted above indicate that the rate of change is determined mainly by the rate of occlusion of the hydrogen. Hence in studying the catalysis of hydrogen and oxygen at hot surfaces it is not really the velocity of a chemical reaction that is being measured, but the rate of a purely physical process. The operation of the law of mass action is masked, and it may be that the chemical combination of the hydrogen and the oxygen at the surface of the catalyst is exceedingly rapid, perhaps instantaneous.

The investigations to which reference has just been made laid the foundations for the introduction of what is known as "surface combustion," in which the catalytic effect of hot surfaces in promoting combustion receives practical application. A homogeneous explosive mixture of inflammable gas and air is made to burn without flame in contact with a granular solid, the latter acting as an accelerator of the combustion, and becoming itself incandescent. In various ways, a description of which would lie outside the scope of these lectures, this surface combustion may be employed for such purposes as the concentration and evaporation of liquids, for heating muffle furnaces, and for steam raising.

In another field, lying far apart from that of combustion, heterogeneous catalysis is found to present various features which are foreign to the law of mass action. Some of the most important catalytic reactions, including many of technical significance, are those which take place under the influence of enzymes. These are catalysts, formed by living organisms and of very complex nature, which promote in a remarkable degree many changes in organic matter. To this class of catalysts belong, for example, invertase, diastase, and the enzymes of yeast.

In certain cases the hydrolysis of carbohydrates under the influence of enzymes is marked by the peculiarity that during the first stages the amount of change is a linear function of the time; i.e., a constant weight of the carbohydrate is hydrolysed in a given interval of time. Such behaviour is not in harmony with the logarithmic mass action formula, $k = \frac{1}{t} \log \frac{a}{a-x}$, which as already shown, does represent accurately the course of hydrolysis of cane-sugar under the catalytic influence of acids.

A case in point is the action of diastase on starch, the earlier portion of the time curve being linear, the later portion being logarithmic in character. This is proved by calculating the velocity coefficient $k = \frac{1}{t} \log \frac{a}{a-x}$,

(1) for each observation from the start of the reaction, (2) for each observation after the linear portion of the time curve has been passed, a new starting-point being chosen. A comparison of two sets of values of k obtained in this manner is given in Table VIII., which refers to the hydrolysis of a 3 per cent starch solution by malt extract at 51–52°.

TABLE VIII.

Time (min.).	k .	Time in min. from new starting-point.	k .
10	0.00498	—	—
20	0.00553	—	—
30	0.00590	—	—
40	0.00620	0	—
50	0.00650	10	0.00842
60	0.00690	20	0.00831
70	0.00706	30	0.00821
80	0.00728	40	0.00837
90	0.00730	50	0.00818
100	0.00732	60	0.00807
110	0.00749	70	0.00822
120	0.00762	80	0.00840
130	0.00779	90	0.00855

(To be continued).

THE COLOUR OF WATER.*

By WILDER D. BANCROFT, Ph.D.,
Professor of Physical Chemistry, Cornell University.

(Continued from p. 200).

"THE Niagara season was over; the chatter of sight-seers had ceased, and the scene presented itself as one of holy seclusion and beauty. I went down to the river's edge, where the weird loneliness seemed to increase. The basin is enclosed by high and almost precipitous banks—covered, at the time, with russet woods. A kind of mystery attaches itself to gyrating water, due perhaps to the fact that we are to some extent ignorant of the direction of its force. It is said that, at certain points of the whirlpool, pine-trees are sucked down, to be ejected mysteriously elsewhere. The water is of the brightest emerald-green. The gorge through which it escapes is narrow, and the motion of the river swift though silent. The surface is steeply inclined, but it is perfectly unbroken. There are no lateral waves, no ripples with their breaking bubbles to raise a murmur, while the depth is here too great to allow the inequality of the bed to ruffle the surface. Nothing can be more beautiful than this sloping liquid mirror formed by the Niagara in sliding from the whirlpool.

"The green colour is, I think, correctly accounted for in the last Fragment. While crossing the Atlantic, in 1872–1873, I had frequent opportunities of testing the explanation there given. Looked properly down upon, there are portions of the ocean to which we should hardly ascribe a trace of blue; at the most, a mere hint of indigo reaches the eye. The water, indeed, is practically black,

and this is an indication both of its depth and of its freedom from mechanically suspended matter. In small thicknesses water is sensibly transparent to all kinds of light; but, as the thickness increases the rays of low refrangibility are first absorbed, and after them the other rays. Where, therefore, the water is very deep and very pure, all the colours are absorbed, and such water ought to appear black, as no light is sent from its interior to the eye. The approximation of the Atlantic Ocean to this condition is an indication of its extreme purity.

"Throw a white pebble into such water; as it sinks it becomes greener, and before it disappears, it reaches a vivid blue-green. Break such a pebble into fragments, each of these will behave like the unbroken mass; grind the pebble to powder, every particle will yield its modicum of green; and if the particles be so fine as to remain suspended in the water, the scattered light will be a uniform green. Hence the greenness of shoal water. You go to bed with the black Atlantic around you. You rise in the morning, find it a vivid green, and correctly infer that you are crossing the bank of Newfoundland. Such water is found charged with fine matter in a state of mechanical suspension. The light from the bottom may sometimes cross, into play, but it is not necessary. A storm can render the water muddy, by rendering the particles too numerous and gross. Such a case occurred toward the close of my visit to Niagara. There had been rain and storm in the upper lake-regions, and the quantity of suspended matter brought down quite extinguished the fascinating green of the Horseshoe.

"Nothing can be more superb than the green of the Atlantic waves, when the circumstances are favourable to the exhibition of the colour. As long as a wave remains unbroken no colour appears; but when the foam just doubles over the crest, like an Alpine snow-cornice, under the cornice we often see a display of the most exquisite green. It is metallic in its brilliancy. But the foam is necessary to its production. The foam is first illuminated, and it scatters the light in all directions; the light which passes through the higher portion of the wave alone reaches the eye, and gives to that portion its matchless colour. The folding of the wave, producing as it does a series of longitudinal protuberances and furrows which act like cylindrical lenses, introduces variation in the intensity of the light and materially enhances its beauty."

The question of the colour of the Mediterranean and of other waters has been studied with a good deal of care by Aitken, whose work seems not to have received the attention which it deserves. Only a lengthy abstract of his paper is available and I quote from that. (Aitken, *Proc. Roy. Soc. Edin.*, 1882, xi., p. 472.)

"The experiments were made with a special view of determining whether the selective reflection or the selective absorption theory gave the correct explanation of the blueness seen in water. According to the selective reflection theory the colour is due to the light reflected by extremely small particles of matter suspended in the water, these particles being so small they can reflect only the short waves of light, or those which belong to the blue end of the spectrum. The other theory explains the colour by supposing that water has a selective absorption for the rays of the red end of the spectrum—that water is in fact a blue transparent medium. Three different methods were adopted of testing the correctness of these rival theories, and all three proved the water of the Mediterranean to be blue by selective absorption, and show that light in passing through the water has the rays of the red end of the spectrum absorbed, and only those of the blue end transmitted. The first method tried was to find out what is the colour of the illumination of submerged objects. This was done by taking a long metal tube, closed at the end with a glass plate, sinking it vertically in the water, and looking through it at white and different coloured objects fixed near the end of the tube. When this was done it was found that a white object appeared of a most beautiful deep and delicate blue at a depth of 6 m. If the selective reflec-

* From the *Journal of the Franklin Institute*, xxvii., No. 3.

tion theory was true, submerged objects would be illuminated with a colour complementary to that reflected by the fine particles, and would therefore appear orange or yellow, the exact colour depending on the amount of green in the reflected blue. If the blue colour of the sky, as generally supposed, is due to the reflection of the blue rays by small particles of matter suspended in the air, it obviously follows that light in passing through our atmosphere must become of a colour complementary to the blue of the sky; and it is asked, may this not be one of the reasons why the sun near the horizon, and all artificial lights when seen at a great distance, appear more or less yellow?

"The second method of experimenting was by looking at a white surface through a considerable length of water contained in a blackened tube. The light transmitted was found to be blue, thus showing the water to have a selective absorption for the rays of the red end of the spectrum.

"The third method was by sinking white and different coloured surfaces under water, and noting the change which took place in the colours. The colours selected were red, yellow, and purple. It was found that these colours when seen through the water changed in the same way as when seen through a blue transparent medium, such as a piece of glass. The white changed to blue. The red darkened very rapidly as it descended, a very small depth of water being sufficient to destroy all the colour. At a depth of about 2 m. a very brilliant red was so darkened as to appear a dark brick red. Yellow changed to green by the water absorbing the red component of the yellow. An orange, as it sunk in the water, appeared to become more and more unripe, while a lemon became quite green. The purple surface quickly changed to a dark blue or violet by the selective absorption of the water. These changes, being all due to the cutting out of the red component of the colours, showed the water to have a selective absorption for the rays of the red end of the spectrum. If the water had been coloured blue by selective reflection, then those test colours would all have appeared deficient in blue when sunk in the water, as the fine particles would reflect and scatter the blue rays. Experiments are described which show that when these colours are sunk in water coloured blue by reflection from small particles, white changes to yellow, while yellow simply deepens in colour, and purple grows redder.

"All these different methods of experimenting show this water to be a blue transparent medium, and that it acts in the same way as a solution of a blue salt or as a blue tinted glass. It is then shown that this selective absorption theory is not enough to account for the different colour phenomena seen in water. A piece of blue glass or a blue solution have but little colour when viewed from the side on which the light is falling, and it seems certain that light will penetrate pure water till it is all absorbed, and the water will look dark and colourless. Something more, and that of great importance, is obviously necessary to explain the different colour phenomena seen in different waters, and in the same water at different times.

"If the water of the Mediterranean, when brilliantly coloured, is examined by means of a concentrated beam of light, it is found to be full of fine solid particles in suspension. It is shown that it is to this dust of the sea—so to speak—that the Mediterranean owes its fine and varied colouring. The particles of this aquatic dust are large, and reflect not only the blue rays, like the supposed particles of the selective reflection theory, but they reflect rays of all colours, and the water, by its selective absorption, strikes down the red rays, and only the blue rays are reflected to the surface and to the eye. These solid particles determine the brilliancy, and the selective absorption of the water determines its colour. The colour and the amount of the suspended particles is then considered. It is shown that the colour of the particles will have a marked influence in the appearance of the water. If the particles are yellow—sand particles, for instance—then a

blue coloured water will appear to be green, as the light reflected by the yellow particles is deficient in the rays of the violet end of the spectrum.

"In the Mediterranean the solid particles are whitish, and all the different colour phenomena are easily explained by the different amounts of the reflecting particles at the different places. Where the colour is deep blue there are few particles in the water, and but little light reflected; and further, the light passes through a great amount of water, and undergoes a great amount of selective absorption before it is reflected to the surface and to the eye. But if there are many particles in the water much light is reflected, and the colour is chalky blue-green, as the light does not pass through so great a depth of water, and is therefore not so deeply coloured, nor has it so many of the green rays cut out as in the water where the particles are few and far separated.

"Colour experiments on a small scale with a solution of Prussian blue and a fine white powder are described. If the solution of Prussian blue is placed in a vessel, the bottom and sides of which are dark and reflect no light, then the coloured solution appears dark and colourless; but if a little of the white powder is added then the solution at once becomes brilliantly coloured. By varying the amount of the powder in the water all the varied colour effects of the Mediterranean can be reproduced, a little powder causing the solution to appear deep blue, and as more powder is added the brilliancy of the water increases, and its colour changes from blue to chalky blue-green.

"The presence and the abundance of white reflecting particles is shown to be a characteristic of all finely coloured waters, and the wave-washed shores of the Mediterranean are shown to be the factories in which are prepared its reflecting particles. The waves, as they beat on the shore, grind up the stones and rocks, and stir up a great amount of fine whitish solid matter, which gives the water along the shore a milky appearance.

"With the assistance of these whitish particles, we understand how it is that the brilliant blue-green of this sea depends so much on the continuance of sea breezes. The longer the wave-mills have been at work the more fine powder has been produced along the shore, and more time given for the particles to be carried seaward, by the wave-mixed and wind-driven waters, and the blue-green which only extended in a narrow band along the shore, when the wind began to blow, is, after a few days of in-shore wind, seen to extend far to sea. We also understand how it is that the colour near shore is so brilliant and so much greener than outside. Near the shore there is a greater quantity of white solid matter in suspension; there is therefore more light reflected, and further, the light does not penetrate through so great a depth of water, and has not so much of the light of the red end of the spectrum cut out, and therefore looks greener than the water outside, the light from which has to penetrate a greater depth of the absorbing medium. The blueness and beauty of the Mediterranean would thus appear to be due to the blue transparency of its waters, coupled with the presence of white reflecting particles, and the variety in its colouring to the amount of the suspended particles at different places and at different times.

"From this we see the important influence which the geological formation of the shore has on the appearance of the water of a sea, as it determines the nature of the solid suspended particles. This is beautifully illustrated by the difference of colouring in the Mediterranean at Mentone and at Cannes. At Mentone, limestone is everywhere abundant along the shore, and this limestone, when ground up by the waves, produces an extremely fine and white powder, which mixed with the water, causes the sea at Mentone to be far more brilliantly coloured than it is at Cannes, where there is but little limestone, and the shore is almost everywhere covered with sand, the debris of the surrounding rocks.

"In the experiments in the Mediterranean it was found that the solid particles were so abundant that they pre

vented the sun's rays penetrating in a direct line to any great depth. This was shown by the illumination of the white surface placed at some distance under the water, and seen through the empty tubes, being the same, whether the surface was turned towards the sun or away from it. It was also shown by the fact that at a depth of 6 m. these solid particles were found to reflect about as much light as a white surface did. These solid particles act like a fog, and, while they stop the light penetrating in a direct line, yet allow it to penetrate much further by internal reflection. The sun's rays get entangled—so to speak—among the particles, and are reflected from particle to particle, becoming a deeper blue with each reflection so that the particles become illuminated with blue light. From this it is obvious that the more transparent the water, and the greater the reflecting power of the particles, the more deeply coloured will the water appear.

"The Lake of Como was the next water visited. A white surface seen through its waters showed it to be as deeply coloured as the Mediterranean, yet the absence of white reflecting particles in its waters and its dark-coloured bottom, cause it to appear comparatively dark and colourless. When a quantity of white reflecting particles are artificially mixed up with the water in this lake a fine blue-green cloud was formed, which remained visible for some time amidst the darker waters, and showed that all this lake required to make it brilliantly coloured was the presence of white suspended particles in its waters. The waters of Como, in their passage from the lake to form the river Adda, change to a fine blue. This sudden alteration in the appearance of the water is shown to be probably due to the addition of fine reflecting particles to the water on entering the river. Lago Maggiore, compared with Como and the Mediterranean, looks greener than either, but reflects more light than Como.

"The Lake of Geneva, whose waters have been so highly praised by all writers, was next visited, and the explanation given of the colouring of the Mediterranean was found to apply here also. Near Bouveret, where the Rhone enters the lake, all the variety of colour phenomena seen in the Mediterranean were repeated. The light coloured muddy waters of the entering river, as they stretched far into the lake, represented the whitish waters near shore in the Mediterranean, and where this whitish stream mixed with the waters of the lake, the bright blue-green of the Mediterranean was reproduced, while further out the waters were deeper blue, rivalling in brilliancy those of the Mediterranean. The work done by the waves along the shores of the Mediterranean in manufacturing the light reflecting particles, is for the lake of Geneva, done by the grinding of the glacier mills and streams of the Rhone valley.

"The silt brought down by the Rhone was found to be composed of clean white particles, like fine white sand. Many of the particles are thin polished plates, and when examined by means of a concentrated beam of light, while in suspension in water, are seen to flash brilliantly in the strong light. This white solid matter brought down by the Rhone is constantly being deposited all over the bottom of the lake, and it is this whitish deposit which gives to the Lake of Geneva one of its peculiarities. The light reflected from the whitish bottom causes the water of the lake, all along the shore, to appear of a peculiar light blue green colour, and enables us to judge of the depth of the lake at depths far beyond that to which we can see the bottom. We can only see a white surface of 15 cm. square to a depth of about 7 m., yet the light reflected from the bottom affects the appearance of the water at depths far beyond 7 m., showing that light penetrates by diffusion in these waters to far greater depths than it can directly. The brilliancy and beauty of the Lake of Geneva would thus appear to be due to the purity and transparency of its waters, coupled with the presence of an enormous amount of white reflecting surfaces, both in suspension in its water and deposited all over the bottom of the lake, the

effect being intensified by the brilliancy of the reflecting particles.

"The colour of the water in Lake Bourget was found to be similar to that in the Lake of Geneva, though at the time it was visited it was slightly more turbid. A white surface could not be seen to so great a depth as in Geneva, and the water, even in the middle of the lake, when examined by means of a concentrated beam of sunlight was found to be very full of suspended light-reflecting particles similar to those brought down by the Rhone. The examination of the water in these lakes was confined to the coloured surface experiments, and to a spectroscopic examination of the internally reflected light. The results were all similar to those in the Mediterranean.

"In the beginning of autumn the sea off the west coast of Scotland, near the village of Ballantrae, and also in Brodick Bay, was visited, and the water examined by means of submerged coloured surfaces, and by means of the spectroscope. The water was here found to be much greener than any previously examined. A large quantity of this water was filtered, when it was found that most of the suspended particles were fine grains of sand. From this it is concluded that the greenness of our northern seas is in part due to the reflecting particles being yellow, and the reflected light, therefore, deficient in the more refrangible rays. These yellow sand particles not only explain part of the greenness of our northern seas, but they also explain their comparative darkness and deadness, the yellow sand particles reflecting so little light. The importance, however, of even these bad reflectors was very evident during the time the observations were being made. It was noticed that the water was much more brilliantly green during and immediately after an inshore wind, and when the filter showed the water to have a good deal of sand in suspension, than after a calm, when many of the particles had settled out. Some water collected about a mile seaward from Ballantrae was examined in a glass tube $7\frac{1}{2}$ m. long, and was found to be of a blue-green colour.

"The water of Loch Lomond was next examined, and found to be a perfect contrast to any previously described, being of a colour nearly complementary to that of the Lake of Geneva. A white surface seen through its waters appeared yellow, and the submerged coloured surfaces showed its waters to have their greatest absorption for the rays of the violet end of the spectrum. Its waters reflect a slightly yellowish light, its spectrum being brightest in the yellow. This water is so deficient in reflecting particles that its brightness is never greater than what we call brown. If it was supplied with abundant reflecting particles Loch Lomond would be a yellow lake.

"Well waters were also examined for colour by placing them in long tubes, and looking through the water at white and at coloured surfaces. The tubes were in pieces, so that they could be fitted up in lengths of 3 m. to 15 m., to suit the transparency of the water under examination. The tubes were fixed horizontally, and at a convenient height for looking through them, and the water to be tested was poured in till the tube was half full, so that by looking through the upper half of the tube the coloured surface could be seen, and through the lower half the effect of the absorption of the water on the colour, and on the brilliancy, of the transmitted light. The transmitted light was also examined by means of a spectroscope.

"The colours of the different waters were found to vary greatly. One sample was of a fine blue, others were green-blue, some green, whilst others were of colours between green and yellow, but all were of colours between blue and yellow. It was observed that the more transparent a water was, the nearer its colour was to blue. Scarcely any light could be seen through 7 m. of any of the yellowish waters, whilst through this length all the bluish waters were quite transparent, and the spectroscope showed that some of the waters transmitted almost the entire light of the blue end of the spectrum, and only stopped the rays at the red end. When one of the bluish

waters was examined in a tube 15 m., or nearly 50 feet long, it appeared of a fine blue-green as transparent as a piece of glass.

"Only a very little relation could be traced between the colour of a water—when tested in long tubes—and its suitability for dietetic purposes.

"The cause of the colour of water has been a frequent subject of speculation. Every substance which has been discovered in water has in turn been suggested as the cause of the colour. When no useful purpose could be given for its presence, it was told off to do the ornamental, and make the water beautiful to the eye. All these speculations assume that the colour is due to some impurity in the water. This, however, is obviously begging the question. It is first necessary to find out whether water has any colour in itself, and what that colour is, before we can say anything about the effect of impurities. As it would be impossible to prepare absolutely pure water, and as we might still be in doubt as to whether any colour seen in purified water was due to the water or to the impurities, the following method of experimenting was adopted: Distilled water was prepared in two sets of apparatus; in one set the condensing tube, the collecting bottle, and the testing tube were all of glass; in the other set they were all made of brass. If the waters prepared in these two sets of apparatus have the same colour, then the probability is that the colour is due to the water, as the impurities will be different in the two samples, and they would probably give different colours. The result was, the colour of the samples of water prepared in both sets of apparatus was the same—namely, blue. This conclusion was further confirmed by preparing another sample of the water, and condensing it this time in a platinum tube. The water so prepared was also found to be of a fine blue. All three samples were almost exactly the same colour as Prussian blue. Standards of colour were kept, with which the different samples of water were compared, both for the colour and for the amount of the colour. As all the different samples of distilled water—after the apparatus was thoroughly purified—had the same colour and amount of colour, it seems almost certain that water is a blue transparent substance, and that the colour in these experiments could not be due to impurities, which must have varied both in kind and in amount in the different samples of water. Further, as the amount of colour in the Mediterranean water, and in the bluish well waters was, as near as could be judged, the same as in pure waters, it does not seem necessary to call in the aid of impurities to account for the blue colour seen in the lakes and seas, the colour being principally due to the water itself, and the different substances in solution, instead of making the water blue, tend to change its proper colour and make it green or yellow.

"The addition of impurities to water seems generally to change its colour from blue to green, or to yellow, though there seems to be no reason why some impurity may not change it to a deeper blue. The selective-absorption of the water remains the same, while the impurities add their selective-absorption to that of the water, and while they change the colour they also decrease its transparency. This explains why it is that the yellow well waters are so much less transparent than the blue. This must necessarily be so, as a very small depth of water destroys the rays which give yellow, and the transparency of yellow waters can only be the transparency of water for yellow light, which is very much less than for blue light. No attempt was made to find out what the different discolouring substances in water are. The task would evidently be an endless one, and of little value.

"The effect of the light reflected from the surface of the water is then referred to. It is shown that when the sky is covered with white clouds, the surface reflection is so strong as to mask the colour of the water, and that when the sky is deep blue the sky-reflected light intensifies and deepens the apparent colour of the water. The importance of the surface-reflected light is best seen when the sky is

covered with clouds, and glowing with a colour different from that of the water, as at sunset when the clouds are richly coloured all over the sky and deeply down towards the horizon. The water will then, especially if calm, appear like a sea of molten metal glowing with sky-reflected light, so powerful and brilliant as entirely to overpower the light internally reflected by the water.

"Pure water having been shown to be perfectly transparent to the more refrangible rays, and as it absorbs the red rays, water, when looked at from the side on which the light is falling, must necessarily be dark, and cannot reflect any perceptible amount of blue light. We must therefore look to the solid particles in suspension in the water as the cause of the light reflected by water, and while the selective absorption of the water principally determines its colour, its brilliancy is entirely determined by the suspended particles. It is shown why it is that though we have waters of many colours, yet we only observe the colour when it is blue or green, and never when it is yellow. Amongst other reasons given is the much less brilliancy of yellow waters, this less brilliancy being due to the less transparency of the yellow waters compared to blue; only the reflecting particles near the surface are active in the yellow water, whereas the particles to a considerable depth in the blue can reflect their light to the surface. This is one reason why Loch Lomond is so much darker than the Lake of Geneva. Loch Lomond certainly has fewer and less powerful reflecting particles than the Lake of Geneva, but it is darker also, because only the particles to a much less depth can reflect their light to the surface.

"The waters of our northern seas, when provided with proper reflecting particles, such as air-bells and white particles, are shown to be much bluer than they generally appear. The brightness and blueness of the waters off the coast of Cornwall are shown to be due to the beaches along this coast being at many points covered with a whitish-coloured sand, which gets mixed up with the water by the action of the waves. As the water of the sea is constantly circulating, it seems impossible that the same water can be one colour at one place and a different colour at another, but we can easily see how the different colours and degrees of brilliancy can be produced by the colour and the amount of suspended matter at the different places—where the water is mixed with whitish particles being bluish, and where mixed with yellow particles appearing greener—whilst its brilliancy is determined by the amount of suspended particles which may be present at the time in the water.

"In conclusion, a lake in the Cordilleras is referred to as combining all the conditions necessary for producing fine and brilliantly blue coloured waters. The traveller in describing this lake says: 'Its waters were of the most extraordinarily brilliant blue I ever beheld.' From the description, this lake is in many respects like the Lake of Geneva. It is provided with an abundant supply of pure glacier water, free from discolouring impurities, but laden with abundance of white-reflecting particles, whose presence is evidenced by a 'white strip' around the lake."

In a letter to Prof. Tait, dated Mentone, April 14, 1882, Aitken (*Proc. Roy. Soc. Edin.*, 1882, xi., 472) says:—

"Since coming here this time I have tested the sea with the polariscope and with the spectroscope. With an instrument by Hoffman, which gives coloured bands with polarised light, I have been able to detect small, but decided indications of polarisation in the light internally reflected by the water, the surface reflection being, of course, cut off when the observation was made. At present I think the polarisation is due to regular reflection from the polished surfaces of some of the particles, which are seen to glance brightly in concentrated sunlight.

"I have also detected an absorption band in the green of the spectrum of the light internally reflected by the Mediterranean water. This band is much more distinct in water where there are but few reflecting particles, and the light undergoes a great amount of selective absorption.

At about a mile from shore, where I could see a white surface 6 inches square at a depth of 16 metres, the absorption band was quite distinct, but became less and less as I approached the shore, where there was more matter in suspension and the water less transparent, but the spectrum more brilliant. I cannot say whether this band belongs to water or to salt, or to what it is due, never having noticed it before; but I never examined water so transparent, and where the light had undergone so much absorption."

Subsequently to Aitken, but apparently independently, Spring (*Bull. Acad. Roy. Belg.*, (3) 1883, v., 55) made a thorough and interesting study of the colour of water. "Water in large masses always appeared coloured to us; but the colour is not always the same and the tints are rich and vary enormously. The Mediterranean is the most beautiful indigo; the Atlantic is sky blue; the Lake of Geneva is famous for the beauty of transparency of its azure waters; the Lake of Constance, the Rhine which flows from it, the Lake of Zürich, and the Lake of Lucerne are just as transparent, but the waters are more green than blue. The little Kloenthaler Sea near Glaris can scarcely be distinguished from the surrounding fields, the water is as near the colour of the grass on the banks. Among the more deeply coloured waters I will mention only the Lake of Staffel near Murnau at the foot of the Bavarian Alps. On the day that I saw it, the water seemed absolutely black, although perfectly clear when seen in thin layers.

(To be continued).

A CONTRIBUTION TO THE CHEMISTRY OF TELLURIUM SULPHIDE.*

By AARON M. HAGEMAN.

A CAREFUL study of any compounds which tellurium is able to form with sulphur is of special interest to the inorganic chemist from a twofold view-point. First, it may serve more definitely to establish the true chemical character of tellurium, and second, it may furnish positive information regarding the possible complexity of that element whose atomic weight has already been more exhaustively studied than any other element known to chemists.

Although Berzelius (*Pogg. Ann.*, 1826, viii., 411) in 1826, reported that two sulphides of tellurium could be prepared by passing hydrogen sulphide gas into acidified aqueous solutions of tetravalent and hexavalent tellurium, respectively, Becker (*Ann.*, 1876, clxxx., 257) showed that the resulting precipitates were not true chemical compounds, since a large part of the sulphur could be extracted with carbon disulphide. The existence of true sulphides of tellurium was therefore questioned.

However, Becker was unable to remove completely all the sulphur from these precipitates by carbon disulphide. He states that a minimum of 3.69 per cent of sulphur is always retained by the tellurium. This phenomenon has attracted the attention of chemists, who have seen a clue to the suspected complexity of tellurium, since the unidentified hypothetical impurity in tellurium must have a higher atomic weight than tellurium, and consequently ought to form a more stable sulphide.

Such has been the assumption of Brauner (*Monats.*, 1889, 456), of Guthrie and Flury (*Zeit. Anorg. Chem.*, 1902, xxii., 272), and of others.

However, none of these workers has been able to obtain positive evidence of the existence of any compound between these two elements, while all attempts to remove completely the sulphur from the precipitate have failed, though Guthrie and Flury have succeeded in reducing the

amount of sulphur retained by the tellurium from 3.69 per cent as reported by Becker to 1.19 per cent.

Snelling (*Journ. Am. Chem. Soc.*, 1912, xxxiv., 802) more recently has reported the isolation of an unstable compound of tellurium and sulphur having the formula TeS . He obtained this compound by passing hydrogen sulphide into an acid solution of tellurous acid of known strength at 0°C . After passing in the gas for twenty minutes, 30 cc. of carbon disulphide which had also been cooled to 0°C . was added and allowed to stand in contact with the precipitate for twenty minutes. The undissolved portion was collected on a filter and analysed. His analysis showed tellurium and sulphur approximately in the ratio required by the compound TeS . Consequently he has stated that at the moment of precipitation one-half of the sulphur is chemically combined with the tellurium as TeS while an equal amount of sulphur exists in the precipitate as free sulphur. He further states that the compound TeS is unstable, decomposing at 0°C . in about four hours, or instantly if heated.

The work about to be described was undertaken in the hope of throwing some light upon the chemical condition of this small amount of sulphur which resists the action carbon disulphide, and to investigate further any true chemical union which may exist between tetravalent tellurium and sulphur. The latter problem was attacked by first carefully repeating Snelling's (*loc. cit.*) experiments in aqueous solution and then carrying out the precipitation of tellurium sulphide in non-aqueous solutions in order to determine whether the medium had any effect upon the composition and stability of the precipitate produced.

Materials.

Tellurous Acid.—Crude tellurium containing, as its principal impurities, small amounts of copper and selenium, was oxidised with aqua regia. The tellurium dioxide thus obtained was freed from nitric acid by gentle ignition, dissolved in concentrated hydrochloric acid, its solution diluted with an equal volume of water, and filtered. From this solution selenium and tellurium were precipitated by sulphur dioxide. After washing with water until free from chlorides, they were fused with KCN at a dull red heat with the formation of potassium selenocyanate and potassium telluride. The fusion product was dissolved in hot water and the tellurium precipitated by means of a current of air, the selenium remaining in solution. This gave very pure tellurium.

This tellurium was dissolved in nitric acid and crystallised twice from dilute nitric acid as the basic nitrate. This was ignited and fused to the dioxide, which, on cooling, crystallised in long, pale yellow crystals. On grinding, a white powder resulted which yielded, upon analysis, by the method of Lenher and Homberger (*Journ. Am. Chem. Soc.*, 1908, xxx., 378), 80.06 per cent Te. Calculated 79.99 per cent. (The figure 127.6 has been used for the atomic weight of tellurium). Tellurium dioxide was converted into tellurous acid by dissolving in hydrochloric acid and diluting the solution with water to the strength desired.

Hydrogen Sulphide.—This gas was made by the action of hydrochloric acid on sodium sulphide. It was washed with sodium sulphide solution and dried with calcium chloride before being used.

Carbon Disulphide.—The carbon disulphide used in the investigation was freed from sulphur by allowing it to stand over copper turnings for at least two weeks. It was then filtered away from any black particles of CuS which had separated and was distilled, only those portions being saved that came over between 44°C . and 48°C . This product left no residue of sulphur on spontaneous evaporation. It was purified as used, no attempt being made to keep the purified product.

Experimental.

A solution of tellurous acid containing 5 per cent free hydrochloric acid was prepared and its exact tellurium

* Abstract of a part of a thesis submitted to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy. From the *Journal of the American Chemical Society*, *all.*, No. 3.

content determined by the Lenher-Homburger (*loc. cit.*) method.

Three samples were taken from this solution and placed in 300 cc. Erlenmeyer flasks. Concentrated hydrochloric acid was added till the samples contained 20 per cent, 10 per cent, and 5 per cent hydrochloric acid. These solutions were placed in a thermostat carefully regulated at 25° C., and after they had attained that temperature, were treated with pure, dry hydrogen sulphide gas until precipitation was complete. In all cases the hydrogen sulphide caused the immediate formation of a dark red voluminous precipitate which increased in volume until most of the tellurium had precipitated, when it began to coagulate in small granules. Simultaneously with this decrease in volume, the colour gradually became darker until the tellurium had quantitatively precipitated as a black mass which settled to the bottom of the flasks. The precipitates were brought upon tared Gooch filters, washed with water containing hydrogen sulphide gas, followed by hot water, then dried in a vacuum over phosphorus pentoxide at room temperature, and weighed. The results obtained follow:—

	Grm.
Weight of Te and S required for TeS_2	0.3035
Weight of Te and S found (20 p.c. HCl)	0.3031
Weight of Te and S found (10 p.c. HCl)	0.3034
Weight of Te and S found (5 p.c. HCl)	0.3038

These results establish two definite facts—First, the precipitate obtained by the action of hydrogen sulphide gas on acid solutions of tetravalent tellurium contains tellurium and sulphur in the ratio 1 : 2; and second, that the concentration of acid has no effect upon this ratio.

The Extraction of Sulphur from the Precipitate.—A precipitate obtained as above from a sample of tellurous acid containing about 5 grms. of Te was transferred to an extraction thimble and extracted in a Soxhlet extractor with carbon disulphide for twelve hours. Then it was freed of carbon disulphide by carefully washing with alcohol, followed by ether, and a sample was analysed for its sulphur content. This was accomplished by treating with nitric acid followed by fuming nitric acid in the cold until oxidation was complete. The solution was evaporated to dryness, the residue taken up in 8 per cent hydrochloric acid, and the sulphur determined by the usual gravimetric method.

The results showed 1.36 per cent and 1.34 per cent sulphur retained by the tellurium, in fair agreement with the results obtained by Gutbier and Flury (*loc. cit.*). By a longer extraction with carbon disulphide these investigators were able to reduce this figure to 1.19 per cent. The experiment shows, however, that a carbon disulphide extraction of comparatively short duration will remove readily all but 1.35 per cent of the sulphur.

Since, then, a small part of the sulphur does not dissolve in carbon disulphide, we may assume three possibilities regarding the chemical condition of this small percentage of sulphur. It may exist in the precipitate in chemical combination with the tellurium or, perhaps, with some undiscovered element more metallic in nature. Such an element would undoubtedly form a sulphide which would completely resist the action of carbon disulphide. Then, again, this sulphur may exist as a form of elementary sulphur that is insoluble in carbon disulphide, though no one appears to have considered this possibility.

To test the two first possibilities, the following experiment was carried out:—A large sample of completely extracted material was treated in a large test-tube with 1 to 1 hydrochloric acid and water and gradually warmed. The test-tube was fitted with a one-holed rubber stopper, and the gases which came off were directed against a filter paper saturated with a solution of lead acetate containing a large excess of sodium hydroxide. Not the faintest coloration which would indicate hydrogen sulphide could be obtained. The experiment was repeated, using stronger hydrochloric acid and also hydrobromic acid of

various strengths, but with negative results. Although these experiments do not prove conclusively that no sulphide exists in the precipitate, it shows that no sulphide which either hydrochloric or hydrobromic acid is capable of decomposing exists in the precipitate.

Amorphous sulphur is known to chemists in one form which is soluble and one which is insoluble in carbon disulphide. The insoluble amorphous modification, frequently known as gamma sulphur, can be produced by decomposing sulphur monochloride with water or by the interaction of hydrogen sulphide and sulphur dioxide. It would not be surprising, therefore, if the latter variety of sulphur were formed here in the decomposition of the tellurium-sulphur precipitate.

The insoluble variety of sulphur may be converted into soluble sulphur by long boiling with alcohol or by subjecting it to a pressure of 8000 atmospheres. The latter method being impractical, the former was resorted to.

The conversion was attempted in the following manner:—A large sample of tellurium sulphur was precipitated as usual and most of the sulphur extracted in a Soxhlet extractor with carbon disulphide. Then the carbon disulphide was removed carefully and the extraction continued with absolute alcohol. By this means the precipitate was subjected to the action of hot alcohol and, at the same time sulphur was dissolved away as rapidly as it was converted to a soluble form. At the end of twenty-four hours of continued extraction, the alcohol had assumed a yellow colour, indicating that some sulphur had been removed from the precipitate. On dilution with water an opalescence confirmed the presence of a small amount of sulphur. The alcohol in the flask was replaced with fresh alcohol and the extraction continued. At the end of the second day the alcohol again became slightly opalescent upon dilution with water. This process was continued for nine days, the used alcohol being replaced with fresh alcohol each day. At the end of this period, since the alcohol showed no trace of opalescence upon dilution with water, a sample was removed and analysed for sulphur. The analysis showed 0.95 per cent and 0.96 per cent of sulphur present in the precipitate. Consequently the extraction was continued for one month. Samples were again removed and the sulphur determined; 0.93 per cent and 0.96 per cent of sulphur still proved to be present in the precipitate.

From these results it is evident that this small amount of sulphur does not exist in the free state, or, if so, in an extremely insoluble and inert form. The manner in which this sulphur exists chemically remains an unsolved problem.

The Non-existence of TeS .—The work of Snelling (*loc. cit.*) at 0° C. has been repeated in detail with only those changes found necessary to increase the accuracy of the results obtained. A sample representing 0.2020 gm. of elementary tellurium was used. The solution was carefully cooled to 0° C. by means of an intimate mixture of pulverised ice and water. The hydrogen sulphide, after being freed from hydrochloric acid gas and dried, was passed through a long coil condenser similarly cooled. After passing the gas into the sample for twenty minutes, 60 cc. of purified carbon disulphide cooled to 0° was added. By a whirling motion the precipitate was completely forced into the carbon disulphide which occupied the bottom of the flask in which the precipitation was made. After standing in the freezing mixture for fifteen minutes, the carbon disulphide assumed a yellow colour and the precipitate became black and granular. The contents of the flask were brought upon a tared Gooch filter which had also been cooled to 0° C. The precipitate was washed with water and dried *in vacuo* over P_2O_5 .

Te in sample, 0.2020 gm.; required for TeS_2 , 0.3035; required for TeS , 0.2527 gm.; weights of Te and S found, 0.2540, 0.2537, and 0.2542 gm.

These results were of special interest since the weights of tellurium and sulphur found were always slightly higher

than the weights required for TeS and considerably lower than those required for TeS₂. A number of such determinations were made, and all tended to show that a compound containing more sulphur than TeS was at first produced.

Assuming that TeS₂ might be produced at first, a series of experiments was carried out in which the time elapsing between the first introduction of hydrogen sulphide gas into the solution and the final removal of the precipitate from the carbon disulphide was reduced from thirty-five to ten minutes. These results seemed desirable since the rapid change in colour taking place immediately after precipitation might indicate the gradual dissociation of the product first formed into its elements. Hydrogen sulphide was passed in for five minutes and the resulting precipitate extracted with carbon disulphide for five minutes.

The results obtained furnished further evidence that TeS was not formed primarily. However, it was difficult to obtain uniform results, and it appeared that all the factors had not been taken into account. The two chief uncertainties were, whether the tellurium was completely precipitated in this length of time and whether the carbon disulphide was in contact with the precipitate a sufficient length of time to remove all free sulphur.

A qualitative test of the filtrate showed small amounts of tellurium still remaining in solution, indicating incomplete precipitation. In order to determine the exact amount of tellurium in each case the Gooch crucibles containing the completely dissociated precipitates were extracted with carbon disulphide until they failed to lose weight. Since all but 1.35 per cent sulphur could be removed, the weight of tellurium in the precipitate was easily calculated.

The use of this method made it necessary to determine whether tellurium itself was entirely insoluble in carbon disulphide. A series of extractions of precipitated tellurium with carbon disulphide in a manner exactly similar to the extractions given the tellurium-sulphate precipitate proved this to be the case. Consequently a series of experiments was carried out using carbon disulphide as the extraction agent. The exact weight of tellurium precipitated in each case was calculated from the weight of the completely extracted precipitate. The precipitates were allowed to stand in contact with the precipitate for exactly five minutes. The results of the experiments are given in the following table:—

Wt. of Te. Grm.	Required for TeS ₂ Grm.	Required for TeS ₂ Grm.	Wt. of TeS ppt. Grm.	S in Te S ppt. Per cent.
0.1956	0.2931	0.2447	0.2884	32.18
0.1968	0.2957	0.2462	0.2891	31.93
0.1990	0.2990	0.2490	0.2943	32.34

Besides explaining why it was impossible to obtain uniform results in the previous experiments, these results furnish more complete evidence that the original precipitate could not have had the composition TeS.

In order to determine whether five minutes was sufficient time for all separated sulphur to be taken up by the carbon disulphide, the following experiment was carried out:—Since hydrogen sulphide has no action on carbon disulphide it was found possible to have carbon disulphide present during the precipitation. This provided for a ten-minute extraction of the greater part of the precipitate. Results of such experiments follow:—

Wt. of Te. Grm.	Required for TeS ₂ Grm.	Required for TeS ₂ Grm.	Wt. of TeS ppt. Grm.	S in Te-S ppt. Per cent.
0.1858	0.2792	0.2334	0.2733	32.02
0.1879	0.2823	0.2351	0.2751	31.70
0.1932	0.2903	0.2417	0.2855	32.32

These results showed that five minutes was adequate for the removal of all free sulphur, since these results were in close agreement with those obtained by the five-minute extractions. Moreover, they appear to warrant the con-

clusion that the first product produced by the action of hydrogen sulphide upon aqueous tellurous acid solutions is not a compound represented by the formula TeS but must be a compound containing a greater amount of sulphur.

One phase of the methods employed up to this point was not entirely satisfactory, namely, the use of a numerical constant in determining the actual weight of tellurium precipitated. An apparatus was consequently devised which permitted a gravimetric determination of the tellurium precipitated, thereby giving a direct instead of an indirect method for the determination.

(To be continued).

PROCEEDINGS OF SOCIETIES.

SOCIETY OF GLASS TECHNOLOGY.

THE Annual Meeting of the above Society was held on Wednesday, April 16, in the Applied Science Department of the University of Sheffield. Mr. W. F. J. Wood, C.B.E., President, took the chair.

After the annual report of the Society had been read, the Officers for the coming year were elected, Mr. S. N. Jenkinson, M.B.E., becoming the Society's new President.

After the formal business had been dealt with, Mr. Wood gave a short presidential address, in which he spoke of the Research Association that had been formed in the glass industry. A provisional committee had been appointed, and at an early date all manufacturers in the Industry would be invited to join the Glass Research Association. Substantial promises had already been received, and it was felt that the scheme would be a great success, especially as it was being looked upon with such favour by the Department of Scientific and Industrial Research.

Mr. A. P. M. FLEMING, O.B.E., Director of Education and Research for the British Westinghouse Co., gave a most interesting and instructive account of Industrial Research in the United States.

Sir FRANK HEATH, Secretary of the Government Department of Scientific and Industrial Research, then addressed the meeting. He pointed out the glass industry had been engaging the anxious consideration of the Government as much, if not more, than any industry in the country since the war began. During the war the Department had been enabled to help the Industry in many ways, and would do so in the future. There was considerable research still to be carried out, but this would cost money, and take time. He could not help feeling that too much dependence upon state aid indicated an unhealthy condition in industry. It ought not to be necessary for any industry to look outside itself for direct and immediate aid in the conduct of its work. That was not the past of British Industry, which was where it is by its own efforts, a fact we were very proud of. It was certain that British Industry would have to save itself by organisation, and work from within. There was very great call from other industries besides that of glass for State Aid in Research. Research was insurance for knowledge, and he appealed to the Research Association to get the best men possible for their work, and then they would be absolutely certain of good results.

Dr. W. E. S. TURNER addressed the meeting. He emphasised the need for research, and showed how it would advantage small firms as well as the great. He gave several examples where money had been wasted and was being wasted for lack of scientific knowledge and supervision. The chemist in co-operation with the engineer was a safeguard in the industry, and he appealed for researches in glass on the pure side as well as the applied.

Before the meeting the Department of Glass Technology was thrown open to members of the Society, many interesting and instructive operations being carried out. Mr. J. B. Davidson, M.Sc., F.I.C., showed the casting of a 2 cwt. Glass Pot.

After the visit of inspection, members of the Society had the valuable opportunity of seeing the Vacuum Casting of a large Glass Pot. The pot when finished was some 38" in diameter, and of the hooded variety. The demonstration was carried out by Mr. B. J. Allen.

In the evening the Society held their first annual dinner in the Grand Hotel; the chief guest was the past President, Mr. W. F. J. Wood, C.B.E., B.Sc. The other guests present included Dr. Ripper (Vice-Chancellor of Sheffield University), Sir Frank Heath, Dr. F. E. Bradley, Mr. A. P. Trotter, Mr. W. Gibbons, Mr. P. V. B. Tippetts, Mr. A. P. M. Fleming, Mr. T. Mortimer Sparks (Commercial Editor of the *Sheffield Daily Telegraph*), Mr. R. Ainger (Commercial Editor of the *Sheffield Independent*).

The next meeting of the Society will be held in London on May 21, when it is hoped that Dr. Walter Rosenhain, F.R.S., will read a paper on "Refractories Research" carried out at the National Physical Laboratory. On the morning of the meeting members will be given the opportunity to visit the National Physical Laboratory.

NOTES.

OSMOTIC PRESSURE AND PREPARED FOODS.—In keeping preserved foods enclosed in skin, osmotic pressure on the membrane of even slightly salt solutions will tend to prevention of putrefaction. An attending phenomena that such is the case is that during sudden fall of temperature there is a distinct exudation of water.—J. C. THOMLINSON, B.Sc.

OSMOSIS AND EMULSIONS.—Osmotic pressure in the presence of emulsions in organic semi-solutions and in pastes gives rise to phenomena, two of which may be described. In the first, solutions of a colloidal character evaporated *in vacuo* may, after standing for some time, contract to a considerable extent, in which neither contraction on cooling or normal evaporation can be advanced as the immediate causes. In the second, organic pastes contained in membranes, on cooling the external surroundings, transuse water by osmosis in quantity, the liquid exuded bearing a considerable ratio to the paste left.—J. C. THOMLINSON, B.Sc.

A new Association called the Technical Inspection Association has recently been formed, which should appeal very strongly to many technical men throughout the Empire who are in any way interested in inspection work. It is the outcome of the Ministry of Munitions Inspection Department, and has been formed for two main purposes:—(1). To maintain intercourse and promote mutual assistance among its members. (2). To conserve and co-ordinate for the national use the experience brought together by the War and generally to develop the progress and standardisation of inspection in the engineering, chemical, and allied industries. Owing to the stoppage of war work the services of large numbers of men, most of whom possess high technical qualifications, and who have spent several years on the inspection of Government contracts, are now available. A list of such members is held by the honorary secretaries, who will be glad to supply particulars to any who may be interested.

THE Hardware and Engineering Supplies Co., Ltd., 16, Water Lane, Great Tower Street, E.C. 3, are manufacturing amber glues in liquid and jelly form, as used by plywood manufacturers, aircraft and cabinet manufacturers, box makers, and bookbinders, superstarch for launderers in liquid form, and soft soaps and soap bases, and desire publications bearing on these industries.

FREDERICK COPE, Consulting Engineer, Southgate Chambers, Wakefield, desires information as to the most efficient plant and up-to-date methods in connection with brickmaking. Also the most modern process for rag carbonising.

THE Board of Trade announce that the Fuel Order, 1918, which controls the sale of wood for fuel, will cease to have effect as from April 30.

It is notified that Messrs. F. Bunn, King's Lynn, G. V. Sedgwick, Middlesex, and B. C. Wilkinson, Reigate, nominated under the 8th Section of the Weights and Measures Act, 1904, have passed the examination provided for under that Section.

A CONSIDERABLE number of merchants and business representatives who formerly lived in Russia are at the present time in the United Kingdom owing to the actions of the Bolsheviks. As a considerable part of the former Russian Empire is now available for trade, it may be that firms in this country would be glad to take advantage of the present exceptional opportunity of obtaining the services of these men, who are especially well qualified to open up trade with Russia. The Department of Overseas Trade would be glad to hear from any firm that desires to be brought into touch with the persons referred to, either immediately or later on, when trading in a more general way can be conducted with Russia. Enquiries should be addressed to the Russian and Scandinavian Section, Sunderland House, Curzon Street, Mayfair, W. 1.

AMONGST the questions which the closing months of the war have brought to everyone's notice there is none of wider interest than domestic service. For although it is the custom to joke over "the servant problem," it comes home vividly to every man and woman in the kingdom. Scoffers may laugh at including elementary science in a cook's training, but how else is she to understand and remember why cold water removes the smell of onions while hot water fixes it; why certain foods should be put down in boiling water while others need cold water; why the contents of some saucepans are to be kept covered and others not? In every department of work the more thoroughly you understand the reason for your routine actions the more interesting they become. For that reason it is always well, where possible, to follow up orders with a brief reason for them—it also fixes the order in the maid's memory and prevents her thinking in some cases that it is purely arbitrary, if it seems at first sight slightly more troublesome than her old method.

NOTES FROM FOREIGN SOURCES.

Yellow Cuprous Oxide.—L. Moser. —The best way to prepare yellow cuprous oxide is by the reduction of Cu^{++} ions in presence of OH^{-} ions by means of hydroxylamine hydrochloride, and the electrolytic method, using a pure copper anode and alkali sulphate as electrolyte. The light yellow product which is first precipitated is very probably cuprous hydroxide, which spontaneously gives up water at a low temperature and is converted into the reddish yellow hydrated cuprous oxide which is amorphous. The dry yellow cuprous oxide is quite stable in air, but it shows a tendency to pass very slowly into the crystalline form. This very slow process can be hastened by heating the amorphous product in absence of air. The yellow cuprous oxide must thus be regarded as the primary metastable form which shows a tendency to pass into the metastable red crystalline modification.—*Zeit. Anorg. Chemie*, 1919, cv., 112.

A very Sensitive Reaction of Copper. Application to the Analysis of Ash and Arable Soils.—L. Maquenne and E. Demoussy.—When a hydrochloric acid solution of an ash, sufficiently concentrated and carefully freed from iron and manganese, is treated with potassium

ferrocyanide, ordinarily the liquid assumes a yellowish pink tint, indicating the presence of copper. But in most cases the coloration is not stable; it rapidly fades, giving place to a turbidity which on standing or centrifugation is resolved into a blackish precipitate tinged with brown or blue, as if the solution still contained iron. The cause of this anomaly appears to be the presence of zinc which is known to accompany copper in the organs of plants. If ferrocyanide is added to a very dilute cupric solution acidified with hydrochloric acid and containing varying proportions of zinc sulphate, the phenomenon can be reproduced, and when the amount of zinc is double that of the copper a blue mass can be separated by centrifugation. The blue coloration attains its maximum of intensity and purity when the zinc is four or five times as abundant as the copper, becoming paler as the proportion is increased. This is one of the most sensitive reactions of copper, and it is only necessary for the solution to be free from nitric acid and iron. To apply the method in practice the ash is heated with sulphuric acid in a quartz capsule, the particles of silica and calcium sulphate are separated by centrifugation and the liquid is electrolysed. After twelve hours the cathode is washed with warm nitric acid and water, the liquid is evaporated, the residue calcined and taken up with hydrochloric acid. Then sulphate of zinc (0.25 mg., i.e., 2 drops of a solution containing 1.104 grms. per cent) and a drop of 10 per cent potassium ferrocyanide are added. If copper is abundant, in which case it would have been visible on the cathode at the end of the electrolysis, a pink coloration, which soon turns blue, appears. If the amount of copper is less than 0.01 mg. the blue coloration appears after some minutes and the depth of the coloration of the precipitate obtained by centrifugation gives an indication of the amount of copper present.—*Comptes Rendus*, 1919, clxviii., 489.

Method of Treating Beryl for the Extraction of Glucina.—H. Copaux.—Beryl usually possesses a composition very close to that corresponding to the formula $\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 3\text{BeO}$, i.e., 67 per cent of silica, 19 per cent of alumina, and 14 per cent of glucina. It is very refractory towards acids, but is acted upon by caustic alkalis, which at a temperature of about 400° transform it into a silico-aluminate of glucina and alkali, which is then readily attacked by acids. This method of opening up the mineral has the disadvantage of necessitating the elimination of the 67 per cent of silica which is present in the gelatinous form. The author has discovered a method of treatment of beryl which depends upon the action of sodium fluosilicate at a temperature of about 850° . Sodium fluosilicate Na_2SiF_6 is a white crystalline powder which is decomposed by heat at about 750° giving sodium fluoride and silicon fluoride, a very active gas which attacks the glucina giving glucinum fluoride $2\text{BeO} + \text{SiF}_4 = \text{SiO}_2 + 2\text{BeF}_2$. The latter then forms sodium fluogluconate with the sodium fluoride $2\text{BeF}_2 + 4\text{NaF} = 2\text{BeF}_4\text{Na}_2$, which is soluble in water. The alumina by an analogous reaction is transformed into sodium fluo-aluminate, which is hardly soluble in water. Thus when the product of the reaction is taken up with boiling water all the glucina goes into solution. To purify the product the aqueous solution is treated with a small excess of boiling caustic soda, which precipitates simultaneously glucina, alumina, and silica, carrying down fluorine. The precipitate is redissolved in sulphuric acid, concentrated to expel the fluorine, and then the glucina is crystallised as sulphate $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$, which is not isomorphous with either aluminium or ferric sulphate, which may be present in small quantities. By this method about nine tenths of the glucina in the mineral is recovered. To determine the glucina in beryl 5 grms. of the finely powdered mineral are mixed with 20 grms. of sodium fluosilicate and heated for thirty to forty minutes to 850° in a graphite crucible. After cooling the powdered mass is taken up three times with boiling water and the aqueous liquid after filtration is made up to

1 litre; 300 cc. are then evaporated in a platinum crucible with excess of sulphuric acid till white fumes are evolved. The mass is then taken up with water and precipitated with ammonia. If iron is present in considerable amount the precipitate is dissolved in acetic acid, and the iron is removed by β -nitroso-naphthol. The filtered liquid is then reprecipitated with boiling ammonia, and the new precipitate, which consists of glucina, a little alumina and silica, is washed, dried, and weighed and then treated with a few drops of hydrofluoric and silicic acids to drive off the silica. After evaporation the alumina is removed by fusing the residue with three times its weight of sodium carbonate, extracting the sodium aluminate with water, and finally weighing the insoluble residue of glucina.—*Comptes Rendus*, 1919, clxviii., 610.

Reagent for and Method of Determining Ozone.—Louis Benoit.—As the phenomenon of fluorescence can be detected optically with great accuracy the author suggests a method of determining ozone based upon its action on fluoresceine. If some cubic centimetres of a very dilute solution of fluoresceine are introduced into a flask of slightly ozonised oxygen, after a few seconds the fluorescence absolutely disappears and the reagent is decolorised. If the solution is more concentrated the fluorescence disappears, but the colour of the reagent is only reduced to pale yellow. Pure oxygen has no effect. The traces of nitrous fumes contained in the air have no effect upon this new reagent, but chlorine does decompose fluoresceine. On the other hand, its presence is very easily detected by other means and the gas can then be eliminated. The same applies to carbon dioxide, which destroys fluorescence when concentrated. The reaction appears to take place between two molecules of ozone and one molecule of fluoresceine, the ratio of the weights being $\frac{96}{332} = 0.29$. The least weight of ozone detectable by this method would thus be one-third of the least weight of fluoresceine which would give an appreciable fluorescence. A Nernst or other lamp giving a very white light is enclosed in a dark box having two contiguous openings in the lid, in which are two colourless glass tubes; one contains the solution of fluoresceine and the other control tube contains distilled water only. The caustic by refraction is observed in each tube, the one containing fluoresceine exhibiting a distinct fluorescence. This method of determining ozone is very sensitive and possesses the advantage of requiring only one solution. The product of the reaction appears to be easily destroyed by heat, but the original fluoresceine is not reformed; the addition of ammonia does not cause the reappearance of the fluorescence, and the final weight of the product after drying is only a very little less than that of the original substance. The product without being explosive appears to be in some way related to the ozonides.—*Comptes Rendus*, 1919, clxviii., 612.

NOTES AND QUERIES.

*. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Particulars and references are desired of the Ogston method for the analysis of citrate of lime.—(Reply to A. C.)

MEETINGS FOR THE WEEK.

- MONDAY, 5th.—Royal Institution, 8. (General Meeting).
TUESDAY, 6th.—Royal Institution, 8. "British Ethnology—The People of Wales and Ireland," by Prof. A. Keith.
WEDNESDAY, 7th.—Royal Society of Arts, 4.30. "The Supply of Electricity," by J. Somerville Highfield.
THURSDAY, 8th.—Royal Institution, 3. "Clutches," by Dr. H. S. Hele-Shaw.
FRIDAY, 9th.—Royal Institution, 5.30. "Chinese Turkistan—Past and Present," by Sir George Macartney, K.C.F.E.
SATURDAY, 10th.—Royal Institution, 3. "Chapters in the Psychology of Industry," by Prof. H. S. Foxwell.

THE CHEMICAL NEWS

VOL. CXVIII., No. 3082.

A CONTRIBUTION TO THE CHEMISTRY OF TELLURIUM SULPHIDE.*

By AARON M. HAGEMAN.

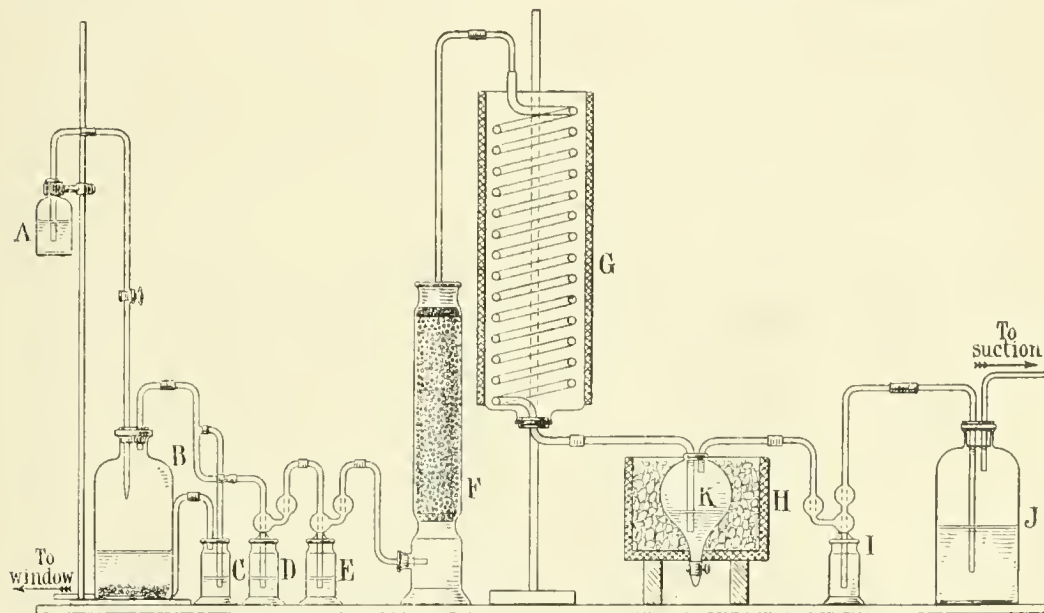
(Concluded from p. 214).

THE apparatus is shown in Fig. 1. The five-litre bottles B contained a supersaturated solution of sodium sulphide. Hydrogen sulphide was generated in this bottle by slowly dropping in 1 : 1 hydrochloric acid contained in the bottle A by means of a syphon and stopcock. It was purified from hydrochloric acid gas by passing through the sodium sulphide wash bottles C and D. After passing through the drying tower F, which contained calcium chloride, the gas was reduced to 0° C. by passing through the coil condenser G, which was completely surrounded by a cooling mixture. After cooling to 0° C. it entered the reaction chamber K, which consisted of a 500 cc. separatory funnel

crucible also was jacketed and surrounded by a freezing mixture.

The advantages of this apparatus deserve mention. The gas was thoroughly cooled to 0° C. before entering the reaction chamber by passing through the long coil condenser surrounded by ice and water. The rate of flow was not great, owing to a fine jet between B and D, but was uniform. The reaction chamber was at 0° C. by being completely surrounded by the cooling mixture. After extraction, the carbon disulphide and that part of the precipitate that had actually been extracted could be drawn away. There was always a small amount of precipitate which remained in a fine suspension in the water above the carbon disulphide which was not extracted, but this never reached the filter. Moreover, the difficulty of filtering two immiscible liquids was overcome. The filter being jacketed with the freezing mixture insured its temperature to be at 0° C., so that at no stage during the operation was the precipitate subjected to any temperature other than 0° C.

Using this apparatus, a final series of experiments was carried out which served as a check on the results previously given. The details of procedure may be described as follows:—A sample of tellurous acid, acidified with hydrochloric acid representing approximately 0.2500 gm. of tellurium, was placed in this apparatus along with



contained in an asbestos-covered iron box with the stem and stopcock protruding through the bottom of the box. The box was completely filled with a cooling mixture for one hour before and during use, thus insuring that all parts of the reaction chamber with which the precipitate might come in contact would be at 0° C. Precipitations were carried out in the presence of 100 cc. of carbon disulphide, into which the precipitate was forced as formed by a constant whirling motion of the box during the introduction of hydrogen sulphide gas. After allowing the precipitate to stand in contact with the carbon disulphide the desired length of time, the carbon disulphide and the precipitate which had collected in it were drawn off through the stopcock on a large Gooch filter. The Gooch

100 cc. of carbon disulphide. Hydrogen sulphide was passed in for three minutes. During this time the reaction chamber was shaken to transfer the precipitate down into the carbon disulphide as formed. At the end of nine minutes the carbon disulphide and precipitate contained in it were passed rapidly through a suction filter consisting of a Gooch crucible fitted with a small disc of filter paper. One minute was thus allowed for the filtration. The suction of the precipitate was continued for ten minutes to remove the last traces of carbon disulphide. The precipitate thus collected was removed from the paper, placed in a P₂O₅ desiccator, and evacuated overnight. A sample of the precipitate was then weighed carefully, oxidised with fuming nitric acid in the cold, and the nitric acid removed by careful evaporation at 80° C. The residue was taken up in 10 per cent hydrochloric acid and the exact tellurium content determined. A short table of results follows:—

* Abstract of a part of a thesis submitted to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy. From the *Journal of the American Chemical Society*, xli, No. 3.

Wt. of Te found. Grm.	Required for TeS ₂ . Grm.	Required TeS. Grm.	Wt. of TeS ppt. Grm.	S in Te-S ppt. Per cent.
0.1824	0.2740	0.2282	0.2682	31.98
0.1650	0.2478	0.2063	0.2424	31.90
0.1168	0.1755	0.1461	0.1708	31.62

These results appear to be in fair agreement with those yielded by the previous method. Hence, since the weights of tellurium and sulphur found far exceed the weights required for TeS, the only conclusion at which one can arrive is that TeS is not formed primarily by the action of hydrogen sulphide on tetravalent tellurium. This is in direct contrast to the results obtained by Snelling (*Journ. Am. Chem. Soc.*, 1912, xxxiv., 802).

A Study of the Conditions Necessary for the Existence of TeS₂.—It will be noted that all data thus far presented have shown that TeS does not exist. Moreover, the weights of tellurium and sulphur obtained have approximated the weights necessary for the compound TeS₂. Furthermore, the colour of the precipitate first produced is invariably a red-brown. At 25° C. the duration of this colour is short, a grey-black colour rapidly developing, accompanied by the coagulation of the precipitate into granules. At 0° C. the precipitate retains its red-brown colour for a considerably longer period. In view of these facts and remembering that ten minutes after precipitation carbon disulphide removes a definite amount of sulphur, it seems justifiable to assume that TeS₂ is first produced, but the affinity between sulphur and tellurium being very weak, dissociation takes place, and the chemical compound separates partially into its elements.

Since the affinity between elements of this character is usually increased at reduced temperatures, a preliminary experiment was carried out at about -40°. A bath of acetone was cooled to -40° C. by the addition of solid carbon dioxide. In it was placed a large test tube containing 50 cc. of carbon disulphide and 20 cc. of tellurium chloride dissolved in concentrated hydrochloric acid. After the contents of the tube had assumed the temperature of the bath, hydrogen sulphide cooled to 0° was passed in. The red-brown precipitate produced was forced into the carbon disulphide as completely as possible. After standing at this temperature for one hour, the precipitate still remained a red-brown and the carbon disulphide still remained perfectly colourless, showing no indication of dissolved sulphur. A second tube containing 50 cc. of carbon disulphide was also cooled to -40° C. To it was added some previously prepared tellurium-sulphur precipitate which had been allowed to decompose at room temperature. This carbon disulphide immediately assumed a yellow colour, indicating the presence of dissolved sulphur.

Although this experiment was only qualitative it indicated that tellurium and sulphur form a stable compound at this temperature, since it was shown that small amounts of sulphur impart a distinct yellow colour to carbon disulphide. If this be true, it was of interest to determine the highest temperature at which this compound was still stable.

For this purpose determinations were carried out at -10°, -15°, and -20°, respectively. In each case the precipitate was gelatinous, thus differing from the precipitates obtained at 0°. In each experiment, too, the extraction with carbon disulphide lasted one hour instead of ten minutes, as previously. During this time the precipitate remained a red-brown colour, showed little tendency to coagulate, and was dissociated but slightly at -10° and -15°. At -20° complete stability apparently existed. The following tables show this to be the case.

It would appear, therefore, that -20° is approximately the highest temperature at which the two elements, tellurium and sulphur, form a stable union.

The Action of Hydrogen Sulphide on Non-aqueous Solutions of certain Tellurium Compounds.—The preceding work has shown that a temperature of -20°, or below, is

Wt. of Te Grm.	Required for TeS ₂ . Grm.	Required for TeS. Grm.	Wt. of Te-S ppt. Grm.
-10°.			
0.1488	0.2236	0.1861	0.2114
0.1165	0.1750	0.1457	0.1691
0.1450	0.2178	0.1814	0.2074
-15°.			
0.1594	0.2395	0.1995	0.2368
0.0882	0.1325	0.1104	0.1299
-20°.			
0.1406	0.2106	0.1759	0.2103
0.1102	0.1652	0.1376	0.1656
0.1132	0.1701	0.1416	0.1709

essential for the existence of a stable compound of tellurium and sulphur in aqueous solution. At higher temperatures the compound undergoes gradual dissociation into its elements. Although such a decomposition can scarcely be regarded as hydrolysis, the influence of the medium upon the formation and stability of this compound is of interest.

Three salts of tellurium were found to have a comparatively wide range of solubility in non-aqueous solvents, namely, tellurium tetrachloride, tellurium acid tartrate, and tellurium acid citrate. Of these three, the tetrachloride showed the greatest range of solubility.

The method of testing the solubility of these compounds in non-aqueous solvents consisted in adding to about 25 cc. of the solvent approximately 1 gm. of the finely divided tellurium compound. The mixture was thoroughly shaken and allowed to stand for at least one hour, after which any remaining solid was separated by filtration. The solvent was carefully evaporated from the filtrate, the residue taken up in dilute hydrochloric acid, and a test made for tellurium with hydrazine hydrochloride. In some cases hydrogen sulphide was passed in directly, the appearance of a red colour proving to be a good qualitative test for tellurium. Assuming that the solubility might in some cases be attributed to small amounts of moisture present in the solvent, when a liquid was found to dissolve tellurium tetrachloride, the liquid was subjected to careful dehydration by shaking with KOH, P₂O₅, or to desiccation by standing over these dehydrating agents until free from moisture. The nature of the liquid determines the method employed. A test of the solubility was then repeated in the absolutely anhydrous reagent, thus insuring that water played no part.

Tellurium tetrachloride proved to be soluble in benzene, toluene, methyl alcohol, absolute ethyl alcohol, normal butyl alcohol, amyl alcohol, benzylic alcohol, xylol, chloroform, and ethyl acetate. In petroleum ether, kerosene, benzaldehyde, acetone, isopropyl bromide, and carbon tetrachloride it was but sparingly soluble, while in carbon disulphide it was completely insoluble. Tellurium acid tartrate was found to be soluble in methyl alcohol, normal propyl alcohol, ether, acetone, pyridine, and acetonitrile. It was sparingly soluble in acetonitrile, aldehyde-cyanhydrin, acetone-cyanhydrin, acetoacetic ester, iso-butyl alcohol, ethyl alcohol, iso-propyl alcohol, fusel oil, acetic anhydride, and benzylic alcohol. The solubility of tellurium acid citrate may be expressed as follows:—Soluble in butyl alcohol, ether, absolute ethyl alcohol, ethyl alcohol, ethyl acetate, and amyl acetate, and slightly soluble in aniline, benzaldehyde, and acetone.

The combined solubilities of these three tellurium compounds offered a large number of mediums in which tellurium sulphide precipitations could be carried out. These solutions consequently furnished data which would either prove or disprove whether the medium in which the precipitation of tellurium sulphide is brought about is an influencing factor.

Hydrogen sulphide was passed into each solution of the tellurium compound in the organic liquid. At room tem

peratures the procedure consisted in precipitating the sulphide, washing it free from hydrogen sulphide with portions of the solvent, dissolving the precipitate in aqua regia, and making qualitative tests for tellurium and sulphur. In many cases, as with acetone, direct addition took place between the hydrogen sulphide and the solvent with the production of extremely obnoxious odours. No further work was carried on in such cases. In a large number of cases, especially where the tellurium compound in solution was the acid tartrate or acid citrate, colloidal solutions were obtained. This was overcome by passing in pure dry hydrogen chloride gas, which usually coagulated the precipitate. When the hydrogen chloride gas reacted with the solvent this procedure could not be used.

A red-brown precipitate at the moment of precipitation was always produced, which appeared identical with the one obtained in aqueous solutions. If allowed to stand at room temperature the precipitate rapidly changed to black, indicating dissociation. The precipitate always gave distinct qualitative tests for tellurium and sulphur.

Since the deportment of the tellurium sulphide precipitated in these solutions was so similar to its conduct in aqueous solution, hydrogen sulphide gas at 0°C . was passed into each of these solutions after they had been cooled to 0°C . As it was practically impossible to make quantitative determinations of the amount of sulphur that could be extracted at this temperature in a given time, and since carbon disulphide is miscible with practically all of these solvents, use was made of the rate of change of colour from red to black. It was difficult at first to determine just when this change in colour had taken place, as it is a gradual one, but practice soon showed that the rate of change of colour of the precipitate in these solutions very closely agreed with the rate of change in colour in aqueous solutions.

A final part of the work consisted in reducing these solutions to -20°C . and passing in hydrogen sulphide which had also been reduced to a low temperature. The red-brown precipitate then remained unchanged in appearance for one hour, which was considered a sufficient length of time to indicate that no dissociation was taking place and that the precipitate was stable at that temperature. In some cases the solutions froze before this temperature could be obtained, and in others so little of the tellurium compound remained in solution at that temperature that comparatively few solvents could be used. The solution of the tetrachloride in ether was very satisfactory.

All of the experiments made in non-aqueous solutions have shown that tetravalent tellurium is precipitated by hydrogen sulphide in these solutions exactly as in aqueous solutions. There is a tendency for the precipitate to separate in the colloidal form, but this may be prevented by the presence of dry hydrogen chloride. If the concentration of the tellurium solution is sufficient this condition is not encountered. The precipitate undergoes dissociation into tellurium and sulphur at the same rate at 0°C . as in aqueous solution, while if the temperature is reduced to -20°C . a stable compound TeS_2 exists between tellurium and sulphur.

Final Conclusions.

The results of this investigation have established the following facts regarding the production and stability of a sulphide of tellurium:—

1. The introduction of hydrogen sulphide into an aqueous tetravalent tellurium solution at room temperatures or below causes the immediate production of a red-brown precipitate represented by the formula TeS_2 . The production of this compound is independent of the acid concentration.

2. At temperatures below -20°C . tellurium sulphide is a stable compound. At temperatures above -20°C ., due to the weak affinity existing between these elements, dissociation takes place. At temperatures approximating -20°C . this dissociation is slow, while at higher temperatures dissociation takes place more rapidly. The

degree of dissociation at any one time or temperature may be determined by the amount of sulphur that can be extracted with carbon disulphide.

3. Dissociation never continues to completion. The dissociated mass extracted with carbon disulphide always retains at least 0.95 per cent of sulphur. This sulphur does not exist as a sulphide of tellurium that is decomposed by hydrochloric or hydrobromic acid of any strength, nor does it exist as a variety of sulphur that is insoluble in carbon disulphide.

4. The compound TeS does not exist.

5. The production of the compound TeS_2 is independent of the medium in which it is carried out. The stability of this compound is solely a question of temperature.

PHYSICAL CHEMISTRY AND ITS BEARING ON THE CHEMICAL AND ALLIED INDUSTRIES.*

By Prof. JAMES C. PHILIP, O.B.E., M.A., Ph.D., D.Sc.

(Concluded from p. 208).

It appears from the figures quoted that if the first portion of the change is left out of account practically constant values for the velocity coefficient are obtained, and it is a fair conclusion that the later portion of the change conforms to the law of mass action. The linear relationship between the time and the amount of change is observed only when the amount of enzyme is relatively small compared with the amount of carbohydrate. Certain recent work indicates that with purified malt diastase the abnormal period of the linear relationship is very short indeed.

The combination of hydrogen and oxygen at the surface of hot porcelain, and the action of diastase on starch, have been discussed in detail in order to illustrate some of the complications that arise in applying the mass action formulæ in cases of heterogeneous catalysis. Another very serious obstacle in this matter is the extreme difficulty, one might almost say the impossibility, of reproducing the catalyst in any desired condition of activity. In heterogeneous catalysis the scene of action lies in the surface layers of the solid catalyst, and it is well known in connection with technical catalysed reactions that the activity of the surface depends, in a very high degree, on the way in which the catalyst has been prepared and on the treatment it has received.

As an illustration of the influence which the previous history of the catalyst may exert on its activity, some observations made by Bone and Wheeler on porcelain surfaces may be quoted. These investigators found that previous treatment of such a surface with hydrogen stimulated quite notably its activity in connection with the combustion of hydrogen and oxygen. Preliminary treatment of the porcelain surface with oxygen appears, on the other hand, to reduce its catalytic activity. These statements are borne out by the figures in Table IX. k , the velocity coefficient, represents, as already explained, the rate at which the hydrogen and oxygen combine to form water. The porcelain surface was the same throughout, and the experiments were performed in the order shown.

TABLE IX.

Previous exposure to—	k
Hydrogen for 24 hours	0.0515
Oxygen for 24 hours	0.0305
Hydrogen for 40 hours	0.0592
Oxygen for 48 hours	0.0373
Hydrogen for 72 hours	0.0622

Normal value for $k = 0.0430$.

* Cantor Lecture (II.). Delivered before the Royal Society of A December 9, 1918. From the *Proceedings of the Royal Society of* LXVIII., No. 3451.

It is noteworthy that the stimulus imparted to the porcelain surface by preliminary hydrogen treatment survived a prolonged exhaustion of the apparatus, but gradually wore off as successive charges of electrolytic gas were circulated over the surface.

The significance of the previous history factor may be emphasised also in relation to one of the most important applications of catalysis on the technical scale, viz., the hydrogenation of oils. The development of this modern

extensive technical developments, but work by others on the same lines showed that if hot oleic acid, in the liquid condition, is treated with a current of hydrogen in presence of a metal catalyst, such as finely-divided nickel, the hydrogen is absorbed and complete conversion into stearic acid is effected. Further, this method is applicable not only to the liquid unsaturated fatty acids, but also to their glycerides; i.e., the liquid fats such as olive, linseed, and fish oils. As a result of this discovery the hardening

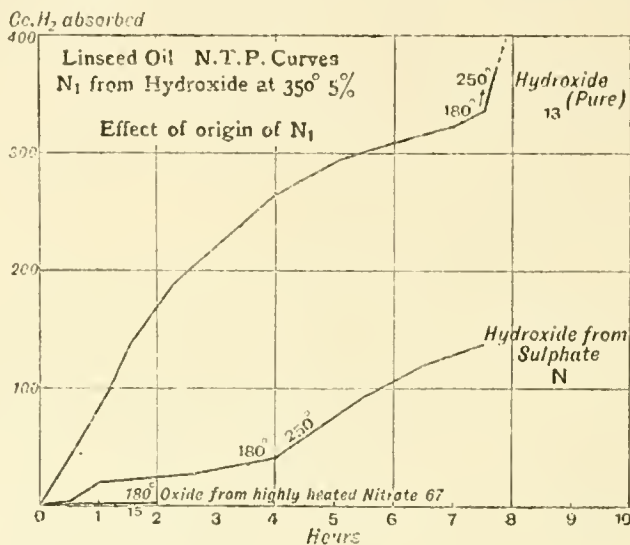


FIG. 1.

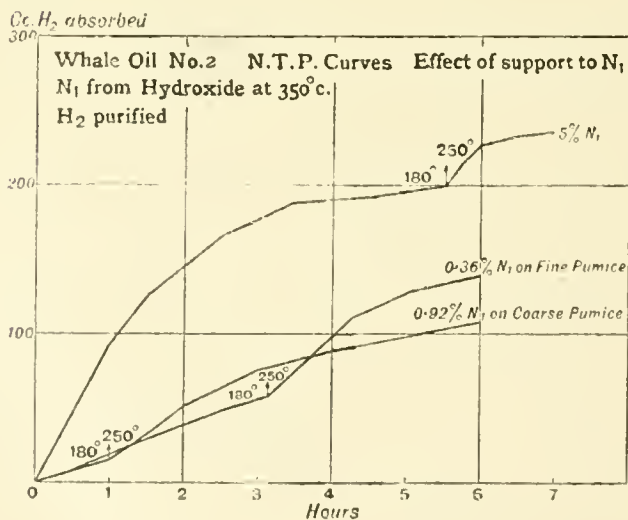


FIG. 2.

industry is based on the classic investigations of Sabatier and Senderens relating to the reduction of organic compounds by hydrogen in presence of reduced nickel. Among other points which these workers established it was shown that the vapour of oleic acid, an unsaturated compound, when treated with hydrogen in presence of nickel at 280–300°, was almost completely converted into the corresponding saturated compound, stearic acid.

This observation, however interesting in itself from the purely scientific standpoint, would scarcely have led to

of animal and vegetable oils has developed into a big industry, the hardened fats obtained by hydrogenation being employed in the manufacture of soap, or, in some cases, for edible purposes.

The very existence of this big industry is bound up with the successful preparation of catalyst metals, more especially nickel, and experience has shown that the activity of this metal is a function of its previous history. The nickel is in almost all cases obtained by reduction, but it turns out that the catalytic efficiency depends on

whether it is the oxide or the hydroxide which is reduced; it varies with the salt from which the oxide or hydroxide is obtained, and with the temperature at which the reduction is effected. The influence of some of these factors is made clear by the diagram shown (Fig. 1, Hehner), from which it appears that nickel prepared from the oxide, obtained in its turn by strongly heating the nitrate, is almost without catalytic activity in the hydrogenation of linseed oil. If the metal is prepared by reducing the hydroxide, obtained from nickel sulphate, there is a distinct improvement, but if hydroxide from nickel nitrate is reduced a catalyst of great activity results. Again, if nickel carbonate is ignited at $400-450^{\circ}$, and the resulting oxide is then reduced with hydrogen at 400° , a product of comparatively poor catalytic qualities is obtained; if, however, the ignition and reduction are carried out at 300° the resulting nickel is highly active.

All this may be regarded as very capricious behaviour on the part of the nickel, but certainly furnishes strong evidence as to the difficulty of reproducing a catalyst of a given degree of activity. That, as already stated, is one of the difficulties in the study of heterogeneous catalysis on quantitative lines.

The degree of sub-division of the nickel catalyst is naturally also an important factor. The hydrogenation presumably takes place at the nickel-oil surface, and the increase of surface which is involved in the progressive mechanical sub-division of a given weight of material may therefore be expected to lead to increased catalytic activity. One common method of securing greater surface extension of the nickel catalyst in the hydrogenation process is to use a porous carrier, such as kieselguhr or pumice. These materials may be impregnated with nickel salt, followed by precipitation of the hydroxide and reduction at a suitable temperature. The effect of such an increase of the contact surface is illustrated by the two lower curves in Fig. 2 (Hehner).

Other efforts to prepare a very finely-divided and therefore presumably highly active nickel catalyst have centred round nickel carbonyl. This compound, when mixed with the oil and heated to about 200° , decomposes completely and gives a fine suspension of the metal which is a very effective catalyst. There is, however, another manner in which nickel carbonyl may be used as the source of an active nickel. This process (Lessing) consists in continuously supplying nickel carbonyl along with the stream of hydrogen which is charged into the hydrogenation chamber. At the temperature which prevails there the carbonyl is decomposed, and the nickel at the moment of liberation presents a maximum surface development, and accordingly a very high catalytic power. It is said that excellent results are obtained even when the proportion of nickel to oil is as low as 1 : 1000.

Like other catalysts the nickel employed in the hydrogenation of oils is very sensitive to certain poisons, among which chlorine and sulphur are prominent. The most important question, however, which has emerged in this connection is whether carbon monoxide is to be reckoned as a "poison" for nickel, and whether, therefore, there is any objection to the use in the hydrogenation process of a hydrogen obtained from water-gas. Opinion appears to have differed on this point, but it now seems to be established that carbon monoxide exerts a marked poisoning effect on the hydrogenation of oils in presence of nickel. This conclusion may be based, for example, on Maxted's experiments in which separate charges of olive oil, each containing 1 per cent of a stock nickel catalyst, were agitated with pure hydrogen or a hydrogen contaminated with a known proportion of carbon monoxide. The volumes of hydrogen (in cubic cm.) absorbed by 10 grms. of oil at 180° in the various cases are recorded in Table X.

An examination of these results shows that the first traces of carbon monoxide have relatively the greatest retarding effect on the velocity of hydrogenation.

The features of heterogeneous catalysis may be further emphasised in connection with a technical process which

is of great and growing importance at the present moment, viz., the oxidation of ammonia. This operation, although it has been known on the commercial scale since about 1902, assumed peculiar significance during the war, for obvious reasons, and it is stated that in Germany as much as 100,000 tons of nitric acid have been produced in this way annually by one process alone.

TABLE X.

Time in minutes.	Pure hydrogen.	Carbon monoxide (per cent).			
		0.25° .	0.5° .	1.0° .	2.0° .
5	86	72	67	58	28
10	143	122	111	93	57
15	194	159	142	116	76
20	248	193	168	136	91
30	348	252	213	164	114
50	515	352	281	215	146

The importance of securing other supplies of nitrates than Chili saltpetre has been recognised in this country, and steps have been taken to put the oxidation of ammonia on a sound technical basis. The United States Government, on its part, has allocated a sum of no less than £20,000,000 to the erection of factories for the production of nitric acid by the oxidation of ammonia.

The conversion of ammonia into nitric acid is effected, as a rule, with a platinum catalyst in the form of gauze or net, through which the mixture of ammonia and air is forced. Quite a good yield is obtained without continuously heating the gauze, but provision may be made for passing an electric current across the gauze, sufficient to maintain it at a dull red heat, say, $600-700^{\circ}$. The reaction is represented by the equation $4\text{NH}_3 + 5\text{O}_2 = 4\text{NO} + 6\text{H}_2\text{O}$, and is accompanied by a considerable evolution of heat.

One of the most remarkable features about this catalytic combustion of ammonia is the very high yield obtained even when the passage of the gases is extremely rapid. Thus, with a mixture of 1 volume of ammonia and 7.5 volumes of air flowing over a 6 in. $\times$ 4 in. gauze at the rate of 20 cubic feet per minute, over 90 per cent conversion can be obtained. That such a brief period of contact of the reacting gases with the catalyst of the order of $0.01-0.001$ second, should be sufficient for the occurrence of the change is indeed very striking.

It has been stated in connection with a description of the converters designed in this country during the war that an output of 1.5 tons of pure nitric acid per square foot of catalyst area per twenty-four hours, with an efficiency of 95 per cent, has been regularly achieved. Hence it has been calculated the output of nitric acid per grm. of platinum is no less than 15 kilograms in the twenty-four hours. This is a remarkable illustration of the first characteristic of a catalyst to which reference has already been made in this lecture, viz., that the amount of the catalyst may be extremely small compared with the quantities of the reacting substances transformed under its influence.

In relation to efficiency, the character and condition of the surface of the platinum catalyst is all-important. Platinum-black and sponge are both too active, and promote an oxidation of the ammonia in another direction, viz., to nitrogen and steam. Massive platinum, on the other hand, with a bright surface, is almost without catalytic activity, and something between this and black or sponge furnishes the most effective surface for the oxidation to nitric oxide.

New gauzes are not very effective catalytically, but are "activated" by passing an ammonia-air mixture at a bright red heat. The bright surface of the platinum becomes dulled in this process, and the catalytic activity increases.

It is, in view of what is generally known, not surprising that the platinum catalyst is very sensitive to certain foreign substances. The ammonia gas must be freed from

possible contaminations as phosphine, silicon hydride, hydrogen sulphide, and acetylene, each of which would "poison" the contact substance. It is found necessary also to filter the gases very thoroughly, since dust, especially if it carries with it particles of iron oxide, has a notably deleterious effect on the platinum. For this reason it is found advisable to avoid contact of the filtered gases with iron pipes, from which traces of oxide might be detached and carried along with the gas current; the converter and the piping which leads to it are therefore suitably constructed of aluminium. Provided that "poisons" are excluded by the precautions just indicated, the "life" of the catalyst is fairly prolonged; it is said that even when the oxidation process is carried on uninterruptedly that platinum gauze remains effective for several months.

The brief review which has been given of some prominent cases of industrial catalysis would lead up naturally to a discussion of the *modus operandi* of the catalyst, but this is somewhat outside the scope of the present lectures. Suffice it to say that, according to one view, the acceleration of a chemical change due to the catalyst is brought about by the rapidly alternating formation and decomposition of an intermediate compound or compounds of which the catalyst forms a part. Thus, for example, the effect of spongy platinum in promoting the combination of a mixture of hydrogen and oxygen is attributed to the primary formation of an oxide of platinum, which in its turn is reduced by the hydrogen, yielding water and the original metal. Similarly, the reduction of the unsaturated organic compounds by hydrogen in the presence of a nickel catalyst is supposed by some to be effected by the preliminary formation of nickel hydride.

Such a chemical view of the mechanism of catalysis can be defended only if the rate of formation and decomposition of the intermediate compound is greater than that of the uncatalysed reaction. In many cases, too, the participation of the catalyst in some intermediate reaction is, to say the least, highly improbable, and in such instances it seems that the catalyst performs some purely physical function. Reference has been made to the catalytic combination of hydrogen and oxygen at hot surfaces, and in this connection it is exceedingly difficult to believe that porcelain acts as a catalyst by undergoing alternate reduction and oxidation. Rather does the surface of the solid in such heterogeneous catalyses appear to provide for some condensation or concentration of the reacting gaseous or liquid substances, the actual chemical change taking place then with high rapidity. Although this view does not presuppose any chemical intervention of the catalyst it does not exclude the possibility that the physical condition of the surface may be altered by the reaction. Indeed, there is evidence in various cases that this actually occurs. When, for example, ammonia is passed over metals at high temperatures and so decomposed, the physical properties of the metals undergo notable alteration, even although no nitrogen has been permanently fixed. Again, the reader may be reminded of the oxidation of ammonia at a hot platinum gauze, in which connection it has already been pointed out that during "activation" the appearance of the platinum surface undergoes a distinct change, passing from a bright condition to a dull one.

Altogether, there is no single theory which can interpret every case of catalysis, and it is certain that in seeking an explanation for the mode of action of the catalyst, both physical and chemical factors must be taken into account.

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THE COLOUR OF WATER.*

By WILDER D. BANCROFT, Ph.D.,
Professor of Physical Chemistry, Cornell University.

(Continued from p. 212).

"BUNSEN was the first to deny that water was colourless. Struck by the greenish-blue tint of the hot water of the Icelandic geysers, he poured pure water into a glass tube two metres long and blackened on the inside. He was able to detect a faint blue under these circumstances and concluded that water is actually blue. The other colours besides blue must then be due to foreign substances or to the reflection of light from a coloured background. Bunsen did not go into details as to the way in which the colour changes would occur. Some twenty years later, Tyndall put forward the view that the blue colour of the sky is due to the scattering of light from numberless colourless particles suspended in the air. This suggested to Soret (*Ann. Chim. Phys.*, 1869, (4), xvii., 517) that the blue colour of the Lake of Geneva might be due to similar causes, and he found that the water sends out light polarised perpendicularly to the refracted rays of the sun. The analogy between the experiments of Tyndall and of Soret is so close that one may claim the existence in the water of transparent particles which may be the cause of the colour. Hagenbach repeated these experiments at the Lake of Lucerne, getting similar results (*Ann. Chim. Phys.*, 1870 [4], xi., 225). The following year, Tyndall himself examined water from the Mediterranean and from the Lake of Geneva, sent to him in London (*Naturforscher*, 1871, iv., 1). When a beam of light was passed through them, it became blue and the blue light was polarised. These waters are therefore not optically empty. These experiments seem to show conclusively that the water itself is colourless, contrary to the opinion of Bunsen; but this is not necessarily true. Soret himself points out that on cloudy days there was not a trace of polarisation and yet the lake was blue. This is sufficient to prove that reflection is not the sole cause of the colour of the water. Further, if the blue of the water were due to exactly the same cause as the blue of the sky, the light transmitted by the water should be a crimson red at least as intense as that which lights up the tops of the high mountains or the thin clouds through which pass the rays of the rising and setting sun. This is not the case, however, as Tyndall himself points out. Also Father Secchi has determined the absorption spectrum of sea-water and finds that the red and yellow are lacking (*Naturforscher*, 1868, i., 149). It is also well known to people who have been down in a diving-bell or who have visited the Swiss grottoes cut in the ice of the Rhone or the Grindelwald glacier that the light is bluish. There is so little red that faces appear livid.

"In 1848, H. St. Claire Deville analysed a large number of natural waters (*Ann. Chim. Phys.* [3], 1848, xxiii., 32), and he observed that the blue waters of the Swiss and the Jura lakes, when evaporated, leave residues which are only slightly coloured, while the green waters of the Doubs and the Rhine contain a considerable amount of organic matter, so that the soluble salts were coloured distinctly yellow when the water was evaporated. From this it appears that the green waters and still more the yellow or brown ones may owe their colour to the presence of a small amount of yellow mud. If pure water is really blue, a small amount of yellow colouring would be sufficient to change the colour to green or even to yellow. This same idea crops up again in a much later paper on the colour of water by Wittstein (*Vierteljahresschrift für praktische Pharmacie*, 1861, x., 342). This chemist analysed the waters of many of the brooks, rivers, and lakes of Bavaria, and thought that he had proved that the brown or yellow waters contain more organic matter and are less hard than the green waters. He explains the

* From the *Journal of the Franklin Institute* clxxxvii., No. 3.

different shades of natural waters by assuming, with Bunsen, that pure water has a blue colour, that the mineral substances dissolved in the water have no effect on the colour, and that the different colours are due chiefly to dissolved organic matter. These organic substances are brown in colour and are essentially humic acids. They are kept in solution by the presence in the water of a sufficient amount of alkali salts. On this hypothesis a water containing very little organic matter would be practically blue, while the blue colour would change continuously to green, yellow, brown, and black as the amount of organic matter increased.

"It is worth while to examine this hypothesis. At first sight it seems an excellent one because it rests apparently on definite facts; but it is easy to show that the hypothesis does not follow necessarily from the analytical data. It is therefore without any firm foundation and does not solve the question. I shall not stop to discuss the question whether the organic matter is brown when it is in solution or whether it becomes brown and even black during the evaporation. In view of the description of the evaporation given by Wittstein, it seems probable that the deep colour is due to the action of heat. Such a discussion would be a waste of time. Let us rather consider the analytical data as shown in Tables II. and III.

("During the evaporation innumerable brown flocks form and become even darker. If heat changes the solubility of the organic matter, it may also affect the colour).

TABLE II.—Brown waters (p.p.m.).

	Organic Matter.	KOH and NaOH.	Ratio.
Ily	37.8	10.1	3.74
Regensee	21.4	15.4	1.39
Rachelsee	43.3	18.4	2.35
Ohe	111.4	12.8	9.0
Steckenbach	55.0	9.5	3.68
Höhenbrunnfliz	59.7	7.8	6.50

TABLE III.—Bluish-green waters (p.p.m.).

	Organic Matter.	KOH and NaOH.	Ratio.
Isaar	39.6	9.8	4.04
Brunnthaler Spring	65.6	4.7	13.97

"These figures show that the colour of the waters stands in no direct relation, either to the amount of organic matter or to the alkali concentration. The green Isaar contains more organic matter than four of the brown waters and also more alkali than two of them. The waters from the Brunnthaler spring show similar relations. It is also worth noticing that Wittstein gives no analysis of a really blue water, and consequently there is no real basis for a comparison. He also makes the general rule that greenish-blue waters are hard because of the small amounts of alkali which they contain while the yellow or brown waters are soft, and then he admits that the rule holds only for running water, because the waters of the Lake of Starnberg are extraordinarily soft although green. I add that the blue waters of the Rhone, where the river flows out of the Lake of Geneva, are also soft, as is shown by the large number of laundries along the river. It is evident that the colour is not different for running and for stationary waters. Wittstein's hypothesis therefore seems insufficient. It may be true, however, for some very deeply coloured waters, because if these really hold a coloured material in solution or in suspension their colour ought to be dark.

Schleinitz attributes the change in the colour of sea-water to the greater or lesser amount of dissolved salts (*Naturforscher*, 1875, viii., 59). He noticed sudden changes in the colour of the sea when he was crossing from Ascension towards the Congo on board the *Gazelle*, in 1875. On August 23, 5° south latitude and 9° west longitude, the sea changed from blue to greenish. On the twenty-fifth it was bluish and on the twenty-sixth, in 5.5° south latitude and 5.5° west longitude, the sea became again deep green, changing to a dirty green and then to a brown as the ship

approached the Congo. Later, on the voyage from the Congo to the Cape, the sea became green, then bluish-green, and finally bright blue. Each time that the sea became greenish Schleinitz found that its specific gravity decreased while there was an increase when the sea became blue again. From this he concluded that the bluest water contained the most salt and that the salt was the cause of the colour. Although this observation led to a false conclusion, it confirms some of the results which I have found, and I shall come back to it again.

"It is worth noting that in the waters of the Lake of Neufchatel, and also in the ice from the lake, J. Brun found an alga which is green, orange, red, or brown, depending on the different phases of its development, and turns black after death (*Jahresbericht über Chemie*, 1880, 1512). Its presence might well affect the colour of the water."

In order to determine the colour of pure water Spring took two tubes five metres long and about four centimetres inside diameter, coated with black on the outside. When distilled water from the laboratory supply was put into the tubes, the colour was a light green, very like that of a dilute ferrous sulphate solution. Some days later the tubes were filled with freshly-distilled water and the colour was a fairly pure sky-blue. After standing about seventy hours in the tubes this water was as green as the first, without having lost any of its clearness. This preliminary experiment shows that the distilled water of the laboratory is far from being pure, and contains substances which undergo changes, in that a blue water becomes green slowly. These foreign substances may be inorganic or organic; it is not impossible that they are living organisms. The following experiment is evidence in favour of this. "The two tubes were filled with distilled water, but one ten thousandth of mercuric chloride was added to one tube. At first both tubes were blue and there was no perceptible difference between them. After six days the water in one tube had become green, while the water containing the mercuric chloride had not changed in colour, and even after three weeks the blue colour was the same. Mercuric chloride was then added to the green tube and after three days a distinct change towards blue was noticeable. At the end of nine days no further change took place, and the water was distinctly bluish-green; but it never returned to a pure blue. Since mercuric chloride is one of the most toxic substances known, especially for minute organisms, there is certainly reason to believe that living organisms are to be found in the distilled water of the laboratory, and that the water also contains the food necessary for the development of these organisms.

"Stas has shown that rain water or spring water, if distilled twice, gives a liquid which volatilises without leaving any residue if evaporated at once in a platinum vessel (*Bull. Acad. Roy. Belg.*, 1860, [2], x.). If this same distilled water is kept several days and then evaporated, it leaves a noticeable brownish-yellow residue, which burns completely at red heat in the air. Stas concluded that distilled water contains volatile organic matter which becomes non-volatile spontaneously in the course of a few days. This conclusion fits in well with my observations. So long as the distilled water contains the dissolved organic matter in a volatile state, the water is blue by transmitted light, but it becomes more and more green as the dissolved matter becomes changed by the action of organisms and ceases to be volatile. A similar fact has also been observed by P. Glan in his studies on the absorption of light (*Pogg. Ann.*, 1870, cxli., 66). He calls attention to the difficulties due to the presence of foreign matter which it is almost impossible to remove. He notes that after distilled water has stood several days in a closed vessel, it lets less light through and appears as though turbid.

"These preliminary experiments show that the distilled water of the laboratory is absolutely unfit for experiments like these, for it changes on standing. Stas has pointed out a method for obtaining pure distilled water (*Mém.*

Acad. Roy. Belg., 1865, xxxv., 110). It consists in distilling spring water with a mixture of manganate and permanganate of potash, taking care to condense the vapour in a platinum cooler. Water prepared by this method contains no trace of non-volatile organic matter either when first distilled or later. I have made use of this method, taking all sorts of precautions. Ordinary water was first boiled with alkaline permanganate for four hours in a glass vessel. It was then distilled twice in an apparatus made entirely of platinum, and was collected in a closed silver flask out of contact with the air. In order to clean the apparatus, three litres of water were distilled and thrown away. Then the first fifth of the final amount of water distilled was used to wash the surface of the silver flask. I have satisfied myself that water thus prepared is volatile without residue. To show this I have polished the inside of a platinum crucible with precipitated and dried silica so as to get a brilliant surface on which the least trace of residue would show. When the water was evaporated in this closed crucible, no visible deposit could be detected on the mirror surface, and I believe that one cannot say that such water contains any non-volatile material.

"When this pure water was poured into the tubes it is hard to describe the purity of the blue colour which was seen. The only thing that could be compared to it is the most beautiful blue of the sky on a clear day at the top of a high mountain when one is far above the mists rising from the ground. When the tubes were allowed to stand for two weeks, no change in the purity of the blue could be detected. The permanence of colour is perhaps a proof of the extreme purity of the water. I have treated this water by the Tyndall method, focussing a magnesium flame on one point of the tube by means of a concave mirror. Unless my imperfect apparatus has led me into error, the luminous cone was scarcely visible in the liquid. It was difficult for me to say whether its path could be detected or not. Whatever one may think on this point, it seems certain that the purest water which one can prepare is a wonderful blue if one looks through a sufficiently thick layer. Is this colour peculiar to the water or is it due to a reflection of the incident light as is the case with the blue of the sky? I think that everybody will reject any hypothesis as to the colour being fortuitous. Under the conditions as arranged, one looked through the water along the axis of the tubes in the direction of the illuminating ray. If the blue were due to the reflection of light from otherwise invisible particles, the maximum intensity of the blue colour should be found in a direction perpendicular to the luminous ray, which is just the opposite to what occurs actually. Further, on this assumption the transmitted light ought to be red or mixed with red, which is not the case, the purity of the blue proving the absence of red. In addition I have made another experiment which seems to me conclusive. If the blue colour of water is not characteristic of this substance and if it is due to the presence of foreign matter coming from the air, it follows that any liquid would be blue like the water if treated in the same way. In other words, there could be no colourless liquid. I have distilled five litres of amyl alcohol for several weeks in a glass vessel and exposed to the air of the laboratory. In spite of this careless treatment, and in spite of the fact that the liquid had taken up a good deal of dust, there was no sign of colour in the tube when the layer was five metres in thickness. Lack of material prevented an examination of a layer ten metres in thickness.

"At first I tried crystallised acetic acid and absolute ethyl alcohol, but these substances were yellow when examined in a five-metre layer. This yellow colour disappeared gradually as the layer was made thinner without showing either green or blue. I am not certain, however, that these substances are really yellow, because acetic acid and ethyl alcohol are apt to contain empyreumatic substances which are very difficult to remove. It seems certain from these experiments that the purest water one can prepare is not colourless but has a blue colour due to

an absorption in the yellow and not to a reflection of the incident light.

"We can now discuss the causes of the different colours of natural waters. Since analysis has not shown in any definite way the presence of green, yellow, or brown matter in the green waters, and since Wittstein himself admitted the absence of any yellow mud in the green water of the Lake of Starnberg, a different line of attack must be chosen. Five litres of pure, blue water were treated with a few grms. of a lime containing no iron and obtained by calcining Carrara marble. This lime water was quite clear after standing for five days. A solution of carbon dioxide in water was added until a precipitate was just barely visible. When placed in the tubes the water was then absolutely opaque. It would not have been any different if ink had been poured into the tube instead of this calcareous water. The water was taken out of the tube, diluted with pure water, and treated with carbon dioxide to precipitate the calcium carbonate and then to redissolve it as bicarbonate. Every now and then the current of carbonic acid gas was cut off and the water was examined in the tubes. The original opacity disappeared slowly, and the light which came through was first brown, then pale brown, yellow, green, and finally the liquid became blue again though with a touch of green after the carbonic acid had been run in for eighteen hours. With the combined action of carbon dioxide and calcium carbonate it is thus possible to reproduce all the colours of natural waters from complete opacity to a greenish-blue.

"As a further confirmation I have prepared a saturated solution of calcium carbonate and carbon dioxide in pure water, which was green when viewed through a five-metre layer. I then placed this in a vacuum tube to draw off some of the carbon dioxide and to cause a dissociation of the bicarbonate, after which the liquid was examined in the tube. Each time this was done the colour became more yellow. The green disappeared soon and finally the tube became opaque. A drop of hydrochloric acid brought back the greenish-blue colour. Similar results were obtained with barium hydroxide and carbon dioxide. With excess of the latter the water became brown, yellow, green, and bluish-green. Using hydrochloric or nitric acid instead of carbon dioxide the colour changes are obtained more rapidly. A solution of sodium silicate containing a little free silicic acid was opaque in a five-metre layer and brownish-yellow when a metre in thickness. When a concentrated solution of caustic soda was added to dissolve the free silicic acid, the yellow colour disappeared. Pure water holding in suspension a little amorphous silver chloride is opaque or yellow, depending on the thickness of the layer. Ammonia dissolves the precipitate and removes the opacity or the yellow colour.

"These experiments warrant the drawing of several conclusions. A luminous beam of given intensity will not pass through a sufficiently thick layer of a liquid holding enough particles in suspension even though these are transparent or colourless. A tube containing suspended calcium carbonate, barium carbonate, silica, or silver chloride may be opaque to diffused daylight and yet let through light from the sun or from burning magnesium. The physical state of the suspended particles does not affect the phenomenon. If one pours water into ethyl alcohol containing a little dissolved amyl alcohol, a persistent turbidity is caused, due to the minute drops of amyl alcohol which do not dissolve in the water. By varying the amounts of ethyl alcohol and water for a given amount of amyl alcohol, one can change the degree of turbidity and make it as small as one pleases. It is evident that each drop of amyl alcohol is liquid and transparent, and yet such a turbid liquid is opaque for a definite thickness of layer and intensity of light; it is yellow if the light is more intense and colourless under a very powerful light. Similar changes take place if the intensity of the light is kept constant and the thickness of the layer decreases. The reason for this is easy to see. When a ray of white light passes through a medium which holds in suspension

an infinity of reflectors, each simple wave forming the white light is reflected independently of the others. If there is not total reflection the intensity of each wave will decrease with increasing thickness of the layer. Since the different colours constituting white light have not the same luminous intensity, the weakest will disappear first and the colour at the ends of the spectrum, the red and the violet, will be eliminated early, while the yellow, which is the most intense to our eyes, will outlast the others though weakened itself. One could probably explain the phenomenon in another way and say that when white light passes through an absorbing medium the yellow is the last to disappear.

"I will add that it is not necessary to have a liquid holding reflecting particles in suspension. A similar phenomenon occurs in the air. Everybody has noticed that the shadow projected by smoke or by condensing vapour on a white background is not merely grey; it always has a yellow-brown colour to which one gives the name of yellow smoke or brown smoke. A liquid holding a colourless substance in suspension appears white solely because of the reflected light. Milky lime water, though very white, is as opaque as ink, and the white colour shows merely that the light which illuminates it does not pass through it.

(To be continued).

ORDERS OF THE MINISTRY OF MUNITIONS.

SEEDS, OILS, AND FATS.

WITH reference to the Seeds, Oils, and Fats Orders dated May 1, 1917, May 9, 1917, and June 19, 1917, the Minister of Munitions hereby orders as follows:—

1. The operation of the said Orders is hereby suspended as on and from April 30, 1919, until further notice.
2. Such suspension shall not affect the previous operation of the said Orders or the validity of any action taken thereunder, or the liability to any penalty or punishment in respect of any contravention or failure to comply with the said Orders prior to such suspension, or any proceeding or remedy in respect of such penalty or punishment.
3. This Order may be cited as the Seeds, Oils, and Fats (Suspension) Order, 1919.

NOTICES OF BOOKS.

Hindu Achievements in Exact Science. By BENQ KUMAR SARKAR. London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. Pp. xiii+82. Price 1.00 dol. net.

This book has been written with the object of providing chronological links between the scientific investigations of the Hindus and those of the Greeks, Chinese, and Saracens, and giving an outlined comparative account of the scientific work of ancient and medieval India. The author believes that the pure mathematics of the Hindus, for example, were in advance of those of the Greeks, and that even some of the European discoveries of the sixteenth, seventeenth, and eighteenth centuries were anticipated by them, while the Hindu inquiries into natural science were not less exact and fruitful than those of the Greeks and medieval Europeans. In support of these contentions he gives in separate chapters short summaries of the chief discoveries of the Hindus, pointing out every case in which they anticipated the workers of other nations. The subjects of the chapters include the various branches of mathematics, astronomy, physics, chemistry, medicine, surgery, anatomy and physiology, natural history, &c., and it is pointed out that India possesses an extensive scientific literature, which is not more contaminated by superstition than European literature of the same epochs.

Petrol and Petroleum Spirits. By WILFRED E. GUTTEN-TAG, Capt. R.A.F., A.R.S.M., D.I.C., Assoc. Inst. M.M., A.M. Inst. P.T. With a Preface by Prof. Sir JOHN CADMAN, K.C.M.G., D.Sc., M. Inst. C.E. London: Edward Arnold. 1918. Pp. xi+135. Price 10s. 6d.

USERS of petrol, such as aeronautical and automobile engineers, have hitherto had some difficulty in getting definite information as to the actual nature and properties of the substance without having recourse to the standard treatises on petroleum, which, being written for the technologist, naturally treat the subject from a highly technical point of view and are more comprehensive and full of detail than is probably required. This book exactly meets the need for a comparatively simple and untechnical account of petrol, and even students of petroleum technology may find that it is useful to them as an introduction to the study of larger works. A short account is given of the properties, origin, and refining of petroleum, and the rectification and refining of petrol are treated in greater detail, while methods of performing routine tests and determining the most important properties of petrol are fully described. Special attention is paid to the discussion of the particular properties which are necessary for various purposes, and the notes and comments on this subject are very valuable. A useful chapter gives some account of the applications of petrol as illuminant, solvent, fuel, anaesthetic, &c., and a bibliography gives the titles of some of the most important English and American books on petroleum and liquid and gaseous fuels.

BOOKS RECEIVED.

Inorganic Chemistry. By JAMES WALKER, LL.D., F.R.S. Pp. viii+236. London: Bell and Sons, Ltd. 1919. Price 5s. net.

T.N.T. By G. CARLTON SMITH. London: Constable and Co. 1918. Pp. vii+133. Price 8s. 6d. net.

Greece before the Conference. By POLYBIUS. With a Preface by T. P. O'CONNOR, M.P. London: Methuen and Co. 1919. Pp. xxvi+120. Price 3s. net.

Annual Reports of the Society of Chemical Industry. Vol. III. 1918. Pp. 408. Issued by the Society of Chemical Industry.

CORRESPONDENCE.

COAL CONSERVATION.

To the Editor of the Chemical News.

SIR,—May I call attention to the important statistics recently laid before the Royal Society of Arts by Sir Dugald Clerk in his paper on "The Distribution of Heat, Light, and Power by Electricity and Gas," and urge that they be taken into careful consideration by the Government before any steps are taken to foster the use of electrical energy as a heating agent.

It is admitted that the provision of an ample and cheap supply of electrical energy for light and power is of great importance to our industries; and in regard to the waste of heat in the coal used for the generation of electricity for those purposes, it does not compare unfavourably with the manufacture of light and power at gas works. The consumer's choice of electricity or gas can here depend solely on cost and suitability.

But the figures given by Sir Dugald Clerk (confirming, as they do, those of Prof. J. W. Cobb in the *Edinburgh Review* for January last) make it clear that a most deplorable and avoidable waste of coal is entailed in the use of electricity as a source of heat. By the use of gas this waste can be avoided, and at the same time the smoke nuisance in our towns and the drudgery in our homes reduced to a minimum.

Broadly it has been shown that to give equal heating or cooking service to the consumer the use of electrical energy as generated to-day entails the destruction of four tons of coal as against one ton at the gas works; and that even if the suggested "super" stations realised the most optimistic hopes of their advocates in regard to coal consumption the comparison would be as 3 to 1 in favour of gas.

Moreover, the use of coal for the raising of steam at electric generating stations means the absolute destruction of all the valuable chemicals recoverable at gas works as by-products, which have so largely contributed to our success in the War, and are vitally important to our industrial and scientific supremacy.

These facts and figures cannot be ignored. They show that the community must depend, in the future as in the past, on both the gas and the electrical industries of the country to play their respective parts in our industrial and domestic economy. Any idea of "doing everything by electricity" cannot be seriously entertained by practical men and women.

I could add much as to the practical drawbacks that would attend the proposed concentration of production in a few "super" stations, some of which were pointed out by the Chairman of the City of London Electric Lighting Company the other day; but my immediate object is to call attention to the gross waste of our national coal resources that would be entailed in the use of electricity as a fuel.—I am, &c.,

D. MILNE WATSON,
President of the National Gas Council.

39, Victoria Street, London, S.W. 1.
April 26, 1919.

EMPLOYMENT OF OFFICERS. CAMBRIDGE UNIVERSITY APPOINTMENTS BOARD.

To the Editor of the Chemical News.

SIR,—In the six or seven years before the War the Cambridge University Appointments Board had been successful in finding places for a considerable number of young Cambridge graduates in industrial and commercial organisations, as well as in professional work. Some of these men were trained in the science, engineering, or agricultural schools; others obtained their places as the result of general ability, apart from any technical training. The object of the Board is to recommend to employers young Cambridge men who are known to us as being possessed of character and ability, and to combine a high standard of selection and a relatively wide field of choice with something like or more than the weight of a private recommendation.

Now that the University is beginning to assume its normal aspect, may I be permitted to remind our friends that we are again able to make recommendations, and to express the hope that many employers as yet unknown to us may be added to the list.

We are faced at the present moment with the problem of placing in employment many young officers who had just completed their University career in 1914, or broke it off in order to fight. It is these, the volunteers of 1914 and 1915, who we are just now especially anxious to place. Some are of exceptional ability. Many, but for the War, would have found their way quite normally to industrial and commercial openings, and by now have made reasonable positions for themselves. They have now to start a year or two older, but often with greatly developed powers, and sometimes with experience which will be of direct use in their future careers. We are in touch also with a certain number of officers rather older than those mentioned above, who had already obtained some experience when the War broke out, but have now to start afresh.

We should be very glad to hear from employers who

will trust us with making recommendations for industrial, commercial, or professional vacancies. Communications from employers are strictly confidential, and information is given to individual candidates only on the employer's instruction. Letters should be addressed to the Secretary, University Appointments Board, University Offices, Cambridge.—I am, &c.,

H. A. ROBERTS, Secretary,
Cambridge University Appointments Board.

Cambridge, May 1, 1919.

THE IMPERIAL WAR RELIEF FUND.

To the Editor of the Chemical News,

SIR,—The claims arising out of the War which are least adequately met are those relating to the widows and orphans of our Sailors and Soldiers. The allowances to widowed mothers, who have to bring up families, hardly provide the necessities of life in these times when food and clothing are so very costly.

The allowances given to the wives and children of the men in the Navy and Army are not sufficient to meet their needs, and a widespread desire has been expressed that these should be supplemented. The Imperial War Relief Fund, which is carefully administered, grants such sums as will increase the allowance to an amount which will more adequately provide for the home.

The objects of the Fund are wide enough to meet the many cases of hardship which are excluded from the scope of other agencies. It seeks to give "Something Extra" to those whose needs are not otherwise met, and who, apart from this Fund, would not receive the consideration they deserve.

Each contributor may recommend cases up to the amount of his subscription. Any donation which you may send for this necessary and patriotic object will be greatly appreciated.

Cheques should be made payable to the "Imperial War Relief Fund, and sent to the Hon. Treasurer, the Marquess of Breadalbane, K.G., the National Provincial and Union Bank of England, Ltd., 15, Bishopsgate, London, E.C. 3.—We are, &c.,

BERESFORD (Admiral), Hon. President.
BREADALBANE, Hon. Treasurer.

NOTES.

THE Ninth Annual May Lecture of the Institute of Metals will be delivered by Prof. Soddy, F.R.S., on "Radio-activity," at Caxton Hall, Caxton Street, Westminster, on Monday, May 19, at 8 p.m.

ROYAL INSTITUTION.—A General Meeting of the Members of the Royal Institution was held on May 5. Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Col. G. Duff Baker, Mrs. Edward Bryce, Mr. C. E. Scott Dickson, Miss H. Newton Drew, Capt. A. Glyn Egerton, the Viscountess Glenconner, Mr. R. Owen Jones, Mr. K. S. Murray, Mrs. Pretymann-Newman, Mr. J. R. Pretymann-Newman, Mr. J. J. Stewart, Mrs. Street, and Mrs. Evelyn Whittard were elected Members. The Secretary announced the decease of Sir William Crookes, O.M., LL.D., F.R.S., and Sir Frank Crisp, Bart., Members of the Royal Institution, and Resolutions of Condolence with the Relatives were passed. The Secretary also announced that His Grace the President had nominated the following gentlemen as Vice-Presidents for the ensuing year:—Dr. H. E. Armstrong, Sir William Phipson Beale, Bart., Dr. J. H. Balfour Brown, K.C., Dr. W. C. Hood, the Hon. Sir Charles Parsons, Sir James Reid, Bart., Sir James Crichton-Browne (Treasurer), and Brig.-General E. H. Hills (Secretary).

ROYAL INSTITUTION.—The Annual Meeting of the Members of the Royal Institution was held on Thursday afternoon, May 1, Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. The Annual Report of the Committee of Visitors for the year 1918, testifying to the continued prosperity and efficient management of the Institution, was read and adopted. The Report of the Davy-Faraday Research Laboratory Committee was read. Twenty-four new members were elected in 1918. Sixty-three Lectures and nineteen Evening Discourses were delivered in 1918. The books and pamphlets presented amounted to about 171 volumes, making with 404 volumes (including periodicals bound) purchased by the Managers, a total of 575 volumes added to the Library in the year. Thanks were voted to the President, Treasurer, and Secretary, to the Committees of Managers and Visitors, and to the Professors for their valuable services to the Institution during the past year. The following gentlemen were unanimously elected as Officers for the ensuing year:—President—The Duke of Northumberland; Treasurer—Sir James Crichton-Browne; Secretary—Brig.-General E. H. Hills; Managers—Dr. H. E. Armstrong; Sir W. Philipson Beale; Horace T. Brown; J. H. Balfour Browne; Dr. J. A. Fleming; Major J. Dundas Grant; Col. John Gretton; the Right Hon. Viscount Hambleden; Dr. Donald W. C. Hood; H. R. Kempe; the Hon. Sir Charles Parsons; Sir James Reid; Dr. J. Emerson Reynolds; James Swinburne; Sir Thomas Wrightson. Visitors—Sir W. H. Bennett; W. R. Bousfield; John G. Bristow, Frank Clowes; Edward Dent; Sir James J. Dobbie; J. Hunter Gray; W. A. T. Hallows; F. K. McClean; W. R. Malcolm; T. C. Owen; Richard Pearce; Sir Edward E. Pearson, Hugh Munro Rose; and Joseph Shaw.

TRADE CATALOGUES FOR PALESTINE.—The Chief Administrator, Occupied Enemy Territory Administration for South Palestine, desires to obtain as many catalogues as possible upon numerous import lines, all of which should find a profitable market in Palestine. Facilities for inspecting these catalogues will be offered to interested parties in Jaffa, Haifa, and Jerusalem, and it is conceived that they will tend in no small measure to the replacement of enemy importation by United Kingdom goods. The main object is to draw enquiry; the question therefore of uncertain catalogue prices, he states, should not debar the sending of trade literature. Actual prices and delivery can be settled by correspondence with the manufacturers and gradual substitution of newer catalogues. Catalogues in the three principal languages of the country, English, French, and Arabic, are much appreciated, and were a great feature in the German pre-war trade propaganda. The following are the principal imports required, and it is suggested that suitable firms should send their catalogues addressed to Headquarters, Economic Section, O.E.T.A., Jerusalem:—Agricultural machinery and implements; Flour mill installations; All kinds of motors; Furniture; Bedsteads; Enamelware; Pottery; Glassware; Lamps; Stationery; Hardware; Ironware; Articles of construction; Book-printing and book-binding machinery and types; Boots and shoes; Drugs and chemicals; Brushes for painting and household; Travelling bags and necessities; Locks; Musical instruments; Typewriters; All kinds of tools; Engines for petroleum and gas; Perfumery.

PUBLIC POLICY AND THE CHEMICAL INDUSTRIES.—The chemical industries of Canada and the United States no less than those of Great Britain and France were born out of the stress of the Great War. Without the successful reconstruction of these industries in the allied countries the war would have been lost, for science and brains, more than muscle, determined the outcome. The rapid establishment of factories producing explosives, miscellaneous chemical works, as well as munition plants and metallurgical works with their necessary laboratories, stands as one of the great miracles of the war. To create

these the owners of industrial plants abandoned their ordinary peace operations and surrendered their rights for the national cause. Some of them found it profitable, while to others the change meant financial loss. To all it meant the breaking-up of old connections and a disruption of business when the war ended. When the creation of the war chemical industries was determined by the Anglo-Saxon nations it was well understood that never again would these nations be placed at the mercy of their enemies in the production of those chemicals that were recognised as key industries. From these cardinal facts it becomes essential to Canada, the United States, and Great Britain that what was demanded as vital to winning the war is now also vital, if the chemical industries are to be safeguarded during the era following the war. Otherwise, our last state will be worse than the first. The preservation and sound development of the chemical and metallurgical industries becomes, therefore, not a question of tariff, but a question of national safety. A number of these established for war purposes at a cost of millions of dollars, now find themselves faced with a serious problem. As they were established by Government action and Government command, so they ought to be secured by Government intervention during the period of reconstruction. This is required by common justice as well as the plain logic of the case. In Great Britain, France, and the United States the situation has been taken in hand by the control and regulation of imports affecting these industries. In Canada there has been a laxness in this control, and a situation has developed which demands a wise foresight if industries established at heavy cost are to be safeguarded during the transition period. Some facts on this situation will be given in another issue.—*Canadian Chemical Journal*, iii., No. 4.

THE POTASH SITUATION.—Deposited here and there over a great layer of rock salt extending through north and middle Germany, lie the beds of potash and other salts which in recent years gave Germany a world-monopoly of the potash supply. The deposits at Stassfurt, extending over a hundred square miles, became famous, as they contain not only potassium chloride, carnallite, a double chloride of potassium and magnesium, and kainite, a compound of magnesium and potassium sulphate, but other valuable salts, the production of which fell into the control of the Potash Syndicate. The syndicate's operations were "bossed" by the government, which regulated the amount allowed for export and the prices at which it should be sold in foreign markets. In 1914, 531,300 tons were allowed to be exported, while 635,000 metric tons were retained for German consumption. In 1904 extensive deposits of potash salts were discovered in Alsace, which to-day are under French control. These deposits are reported to contain a billion and a half tons of raw material, equal to 300,000,000 tons of pure potash. This is in the form chiefly of muriate of potash, easier to purify than the salts at Stassfurt. Owing to the destruction of machinery by the Germans during the war it will take a year or more to put the Alsace potash mines in proper working order, but when that is done the annual output will be 800,000 tons, which will be about ten times the production that was permitted to the Alsatian mines by the Germans before the war. In other words, the world will get from Alsace alone nearly 300,000 tons more than was allowed before the war. Meantime, as the result of the cutting off of German supplies during the war, there has been a keen quest for other sources of potash. A considerable amount has been, and will continue to be, recovered from the flue dust in cement works. Some has been made from the seaweed, kelp, but while this and some other sources have been used during the period when potash rose from 40 to 45 dols. a ton up to 400 and 450 dols. a ton, they are not likely to be much in demand when the product drops below 100 dols. a ton. Important deposits of potash salts have been found near the borders of Abyssinia, in the Italian district of Eritrea, and these reached an output last

Year of 20,000 tons. Deposits also have been found in Spain at Cordova, Luria, and other places, and the brine and salt lakes of Nebraska and California are now worked for their potash contents. A great future source of potash exists in the felspar rocks in which Canada is rich, but the chemical problem involved in producing it from this source is yet to be solved on a commercial scale. On account of the fall in prices the present is a critical time for potash producers in America. It is reported that 100,000 tons of potash produced in Nebraska are in storage warehouses awaiting sale. The total production from the Nebraska is about 220,000 tons a year, equivalent to 50,000 tons of pure potash; the production of the California works at Searles Lake being about 10,000 tons of "actual" potash. Kelp yielded last year a little over 10 per cent of the domestic production of potash in the United States. Foreign potash cannot be brought into Canada or the United States in time for this year's use on the land, so that if the existing stocks are freely drawn on it would be better for the farmers in securing greater production, and would give a chance for some branches of the new industry to survive. The American War Trade Board announces that no potash from Alsace will be available on this side before June next—and even then the imports are to be regulated by licence. By these means it is expected that a collapse in prices will be avoided.—*Canadian Chemical Journal*, iii., No. 4.

MEETINGS FOR THE WEEK

Monday, May 12.

Royal Geographical Society. "Crete—Its Scenery and Natural Features," by A. Trevor Battye.
Ceramic Society, 7.30.

Tuesday, May 13.

Royal Institution, 3. "British Ethnology—The People of Wales and Ireland," by Prof. A. Keith.
Royal Horticultural Society, 3. "Bottling and Drying," by Vincent Banks.
Royal Photographic Society, 7. "Development Papers and Desensitisers," by W. C. Mann.

Wednesday, May 14.

Royal Society of Arts, 4.30. "Railway Transport in the United Kingdom," by H. Kelway-Bamber.
Institution of Electrical Engineers, 6. "Wireless in the Royal Air Force," by Major J. Erskine Murray.

Thursday, May 15.

Royal Society, 4. (Election of Fellows). "Area of Surfaces," by Prof. W. H. Young. "Change of the Independent Variables in a Multiple Integral," by Prof. W. H. Young. "Chemistry of Coal—Part I. Action of Pyridine upon the Coal Substance," by Prof. W. A. Bone, F.R.S., and R. J. Sarjant. "A New Method of Weighing Colloidal Particles," by Prof. E. F. Burton. "Value of the Rydberg Constant for Spectral Series," by W. E. Curtis.
Royal Institution, 3. "Intensive Cultivation," by Prof. F. Keeble.
Royal Society of Arts, 4.30. "Soil Deficiencies in India, with special reference to Indigo," by Prof. H. E. Armstrong.
Institution of Electrical Engineers, 6. "The Telephone Service of Great Cities, with special reference to London," by E. A. Laidlaw and W. H. Grinstead.
Chemical Society, 8.

Friday, May 16.

Royal Society of Medicine (Otolaryngology Section), 5. (Annual Meeting).
Royal Institution, 5.30. "Subantarctic Whales and Whaling," by Dr. S. F. Harmer.

RESEARCH FELLOWSHIP.

SCOTTISH TANNERS' FEDERATION.—

Applications are invited for Post as RESEARCH FELLOW to the Scottish Leather Trade. Salary £400 per annum with a financial interest, to be mutually agreed upon, in discoveries of commercial value.—Address, S. T. F. CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

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Applications (endorsed "Analytical") must be upon the form provided, and must reach me not later than FRIDAY, MAY 30th.

Canvassing in any form will be a disqualification.

N. J. HUGHES HALLETT,
County Offices, Derby. Clerk of the Derbyshire County Council.
Dated this 1st May, 1919.

UNIVERSITY OF MANCHESTER (FACULTY OF TECHNOLOGY)

MANCHESTER MUNICIPAL COLLEGE OF TECHNOLOGY

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Conditions of appointment and form of application may be obtained from the Registrar, College of Technology, Manchester. The last day for the receipt of applications is 14th June, 1919.

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J. C. MAXWELL GARNETT,
Dean of the Faculty.
Principal of the College.

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THE CHEMICAL NEWS

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ON ACQUIRED RADIO-ACTIVITY.*

By Sir WILLIAM CROOKES, O.M., LL.D., D.Sc., &c.

Experiments with Cathode Rays.

1. ABOUT forty years ago I sealed in a vacuum tube a yellow diamond cut as a brilliant. This diamond was chosen because it phosphoresced in the dark after exposure to bright sunshine—it also phosphoresced slightly under the influence of ultra-violet light. In the vacuum tube, as the anti-cathode, it emitted a brilliant yellowish white light giving almost as much light as a candle. It was often exhibited to illustrate the glow of a diamond under the influence of cathode rays *in vacuo*; scarcely a week passed without the vacuum tube containing the diamond being exhibited to friends. It was by far the most attractive tube in my collection. After forty years of hard work the diamond has become much discoloured. It was of interest to see if the repeated bombardment, as the anti-cathode, in the vacuum tube had conferred radio-activity on the diamond. Accordingly I opened the tube, quickly removed the diamond, and in the dark put it on a sensitive film, a thin sheet of black paper intervening. Over the diamond was placed a pad of cotton-wool and a weight, to prevent the stone from shifting its position. After nine days' contact the film was developed. An exceedingly slight action could, with difficulty, be detected, showing that the off and on action for forty years had conferred practically no radio-activity on the diamond.

2. A sensitive electroscope was now made, with sulphur insulation. The fall of the leaf was observed with a small telescope having a photographed scale. The normal fall due to natural leakage was 5° in 165 seconds. A piece of a thoria gas mantle caused a fall of 5° in two seconds, and radio-active diamonds caused a fall in from two or three seconds to a fraction of a second. Tested in this instrument I found this special diamond to be entirely devoid of action.

Action of Cathode Rays on Diamond.

3. On one occasion when M. Moissan was in my laboratory I darkened some diamonds by means of cathode rays. One of these he took away, and subsequently reported the result of his experiments to the French Academy (*Comptes Rendus*, cxiv., No. 13, p. 653, March, 1897). He heated the diamond to 60°C in an oxidising mixture of potassium chlorate and fuming nitric acid, prepared from monohydrated sulphuric acid and potassium chlorate fused and free from moisture (9, 12, 32). The action on the dark layer is very slow, requiring at least eight or ten days for its complete removal. There is at first produced graphitic oxide which at an increased temperature yields pyrographitic acid easily destroyed by nitric acid. Hence the variety of carbon which coated the diamond is graphite. The transformation of diamond into graphite requires the temperature of the electric arc, and the higher the temperature at which it is formed the greater is its resistance to oxidation. M. Moissan came to the conclusion that the temperature reached by the surface of the diamond blackened in my radiant matter tube was probably about 3600°C .

4. Six diamonds—having different degrees of phosphorescence under cathode rays—were tested in a Becquerel phosphroscope to see if the order of intensity of the residual phosphorescence due to illumination with an arc light was the same as the order under cathode rays. All had a slight residual phosphorescence, but the order of intensity differed in the two cases.

Action of Cathode Rays on various Mineral Substances.

5. For many years I have experimented on the changes produced in ordinary and quartz glass and various crystals by exposure to radium emanations and rays.

Considering the identity of the cathode discharge in a high vacuum tube with the β rays from radium, experiments were started to ascertain if the cathode rays would confer radio-activity in various solid bodies submitted to its influence. A vacuum tube was prepared with a removable window at one end to allow the contents to be exchanged for other bodies. In the tube were placed pieces of uranium glass, a crystal of ruby, a crystal of garnet, a piece of quartz, a plate of platinum and one of gold. The tube was exhausted to a high vacuum just short of the non-conducting point. On excitation the whole tube was filled with the green glow of phosphorescent glass, the ruby and uranium glass became very phosphorescent, the other bodies remained quite dark. After an hour's exposure to the cathode discharge the tube was opened, the objects quickly removed in the dark and placed on a sensitive film; the upper sides that had received most bombardment being placed downwards on the film. They were kept thus for eighteen hours and the film then developed. There was absolutely no impression of any of the bodies on the film. Thus it appears that the cathode stream will not confer radio-activity on the above-named bodies.

Action of Cathode Rays on Phosphorescent Bodies.

6. Experiments were next tried to see if earths and compounds which became strongly phosphorescent under the influence of the cathode discharge would thereby become radio-active. Some ignited yttrium sulphate, in the condition most sensitive to the cathode rays, and giving under their action a phosphorescent glow with a discontinuous spectrum, was pressed tightly into a shallow aluminium tray and exposed for an hour to the discharge in the vacuum tube. It was then removed and immediately covered with a sensitive film pressed down with a slight weight. After forty-eight hours in total darkness the film was developed. Only a very slight image of the yttria was visible. This result does not prove that the cathode stream had rendered the yttria radio-active, for there is always a residual glow in the yttria in these circumstances; it is not unlikely that the light of this glow, acting for the first hour or so of the forty-eight, might have been strong enough to impress the film (7).

7. Three shallow trays were filled—one with phosphorescent calcium sulphide, another with zinc sulphide, and a third with platinumocyanide of barium. After subjecting them to the cathode stream in the above manner, they were removed and covered with a sensitive film, and kept in darkness for twenty-four hours. On development only an impression of the zinc sulphide was seen. As this sulphide also has a certain amount of residual glow after exposure to the cathode rays it is probable that the photographic action is only the result of this glow (6).

Action of Radium on Diamond.

In June, 1904 (*Roy. Soc. Proc.* lxxiv., 47), I read a paper before the Royal Society on the action of Radium on Diamond.

8. A few years later I repeated the original experiment, exposing two New South Wales diamonds to the action of the radium rays and emanations for a longer period. The diamonds selected were of an identical pale yellow, devoid of radio-activity. A quartz tube containing 15 mgrms. of pure radium bromide was well exhausted and sealed before the oxyhydrogen blowpipe. One of the diamonds was put close to the tube of radium and kept in its place with a piece of gummed paper. The other diamond was put away in a cabinet and kept far away from any radium compound. The two diamonds were thus left for a little more than six months. At the end of this time they were examined. No appreciable difference could be detected

* A Paper read before the Royal Society. From the *Philosophical Transactions of the Royal Society*, ccxiv., A, 521.

in the colour of the two diamonds—the one that had been close to the tube of radium bromide not being darker than the one which had been away from radium the whole time.

Coloration of Diamond by α -Ray.

9. The diamond was now enclosed for seventy eight days in a tube containing radium bromide; at the end of the time it had acquired a bluish green colour. It was then heated for ten days in a mixture of fuming nitric acid and potassium chlorate so as to dissolve off any outer skin of graphite which might have contributed to the colour (3, 12, 32). The treatment brightened its appearance but did not alter the colour. The diamond was next put on a sensitive photographic film and kept there for twenty-four hours. On developing, a strong impression was seen.

β - and γ -Rays produce Phosphorescence.

10. This experiment shows that the alteration of the colour is not due to the phosphorescent state of excitement to which the diamond had been constantly subjected during eight weeks. The colouring action is cut off by a thin screen of quartz, whereas the phosphorescing action is kept up by rays which pass through quartz. It is therefore evident that the coloration is due to the α -rays, or atoms of helium, shot from the radium compound (26, 29, 33). The phosphorescence is produced by the β - or γ -rays (19, 26, 43), which readily pass through glass and quartz.

Persistence of Acquired Radio activity.

11. The acquired radio activity of diamonds persists for a longer time than I have been enabled to measure, and resists the most violent treatment I have applied to them.

A large brilliant cut diamond of pure water assumed a fine green colour after having been kept for sixteen months (from May, 1904, to Sept., 1905) in a bottle and covered with powdered radium bromide. At the end of that time it was highly radio-active. This diamond has been carried about in my pocket, off and on, since 1905, and has been tested on a sensitive photographic film at intervals of a year or more. No appreciable difference in its radio-activity can be detected from that which it possessed when first removed from the radium bromide in Sept., 1905. Examined at the present time, nine years after its removal from the bottle of radium bromide, it is luminous in the dark, it rapidly discharges a sensitive electroscope when held near it, and produces scintillations on a zinc sulphide screen as if it were a radium compound.

12. A diamond of good water was selected from a stock of inactive stones, and put in a tube of radium bromide for seventy-eight days. At the end of that time it had assumed a greenish colour, and was highly radio-active. It was then heated to 50° C. in a mixture of fuming nitric acid and powdered potassium chlorate for ten days, the acid mixture being daily renewed (3, 9, 32). The only effect of this acid treatment was to remove a slight dull darkening on the surface, and to render the green tint more brilliant.

After well washing and drying it was put on a sensitive film for five hours. On developing it was seen that the stone had made a good impression on the film.

13. The stone was then sent to a diamond cutter to be cut into a brilliant. On receiving it back it was quite white and free from trace of colour. The stone was then placed on a sensitive film and kept in darkness for twenty-two hours. On developing no impression was apparent, although, before cutting, the active diamond had impressed a film in five hours (12, 16).

Effect of Heat on Induced Radio-activity.

14. A New South Wales diamond which had always been kept away from radium salts, was tested in the electroscope (2) and found to give a fall in two seconds, the natural leak being 180 seconds. The stone was then put in a silica crucible and heated in an electric tray fur-

nace until visibly red. No change was observed. After 5 minutes—at, say, 700° C.—it was allowed to cool. The time of discharge in the electroscope was found to be six seconds.

15. The diamond was then packed in a silica crucible with graphite and heated with a Meker burner to 700° C. several times, cooling and testing the diamond each time when cold.

Heated to 700° C. for 10 mins., and cooled, time of fall = 6 secs.

Heated to 700° C. for 15 mins., and cooled, time of fall = 10 secs.

Heated to 700° C. for 20 mins., and cooled, time of fall = 10 secs.

Heated to 700° C. for 20 mins., and cooled, time of fall = 30 secs.

It was now left for the night, and measurements resumed next day.

Heated to 700° C. for 60 mins., time of fall = 9 secs.

Heated in new graphite for 30 mins., time of fall = 7 secs.

New graphite again used.

Tested again after 48 hours, time of fall = 4 secs.

Heated to 700° C. for 30 mins., and allowed to cool for 2 hours, time of fall = 2 secs.

The diamond after the last measurement (2 secs.) was laid on a sensitive film and kept in the dark for twenty-one days; on development it gave a good image.

This experiment shows a temporary loss of activity by the heat treatment followed in a short time by complete recovery.

16. A Kimberley diamond, rather flat, octahedral shaped, was kept in a bottle of dry radium bromide for some weeks until it was quite green. By means of a steel wheel fed with diamond dust part of one face was cut away, and the surface of an adjoining face was just removed, the adjoining corner thus being freshly exposed diamond crystal. It was put on a sensitive film in such a position that it could be subsequently examined and compared with the developed image, so that the active portions of the surfaces, natural and ground off, could be seen. It was allowed to act for five days, when the film was developed. The result indicated very decidedly that where the surface of the diamond had been removed it was no longer radio-active (13).

Experiments with a very Active Diamond Crystal.

17. A fine crystal of diamond from Kimberley which had been kept in a bottle of radium bromide for some months was tested on a sensitive film and in the electroscope. It was found to be highly active, and was set aside for further experiments. It was luminous in the dark, quickly discharged the electroscope, and caused an inactive diamond held near it to phosphoresce. It was put on the surface of a screen coated with small crystals of barium platinocyanide, and caused scintillations the same as on a blende screen, but feeble (11, 26, 27, 30, 33).

18. A blende screen was made by coating a glass slip with very sensitive zinc sulphide. This was laid on the diamond, the ZnS side next the diamond; the scintillations were easily seen through it in all their characteristic appearance, with concentration at the edges and corners. A piece of aluminium sheet, 0.06 mm. thick, was moved about between the screen and crystal of diamond, and there was no doubt whatever that the aluminium stopped all the scintillations. It was absolutely dark where the aluminium covered the crystal.

19. The diamond (17) was then held in contact with the card back of a platinocyanide of barium screen. The luminous patch due to β - or γ -rays, or to both, was quite evident, moving about as the diamond was moved. The sheet of aluminium foil used in the former experiment (0.06 mm. thick) was put between the crystal and the back of the screen, and there was little, if any, diminution in

the luminosity. It is therefore quite certain that the radio-active diamond gives off other rays besides α rays, and that the rays can penetrate aluminium 0.06 mm. thick and the card back of the screen.

20. The diamond (17) was put into various fluorescent solutions (uranine in water, Silberard's β -nitroso-dimethylanilinenaphthaline compound, and quinine sulphate). It did not occasion the slightest fluorescence, although its own faint luminosity could be seen in the liquid.

21. The active diamond (17) was cemented to a plate of glass, and six small pillars of lead cemented round it the same height as the stone. The whole was inverted on a sensitive film, and kept in the dark for 2.25 hours. Another experiment was then tried with the same apparatus, only altering the position of the crystal so that the lead pillars were opposite the angles of the crystal. The exposure in this case was 6.5 hours. The pictures on development showed a strong radiation extending some distance round the diamond (six or eight diameters) and the lead pillars showed strong shadows.

22. The same experiment was repeated three times with the interposition of one, two, and three thicknesses of aluminium foil 0.01 mm. thick, each was exposed the same time (two hours), and all were developed together. Each showed strong action near the diamond. One thickness allowed the shadow of the lead pillars to be easily seen. Two thicknesses showed the shadow with difficulty, and three thicknesses only showed the shape of the diamond itself.

23. The crystal (17) was removed from its circle of lead pillars (21). A small cell of brass tube 0.5 inch in diameter had six slots cut in it with a file. The diamond was mounted in such a position that the three corners of the triangular surface that touched the film should come opposite three of the slots. These experiments show that the diamond is giving off β -rays copiously.

γ -Rays from the Radio active Diamond.

24. The diamond (17) crystal was fixed with its sharpest point upwards in a small thick cell of brass. Exactly over the point was a small hole 0.5 mm. in diameter and 5 mm. long. On the top was a piece of sensitive film enclosed in black paper. The whole was kept in the dark for three hours, when a fair image of the hole was obtained on development. The apparatus, with another sheet of sensitive film in it, was fixed between the pointed poles of a powerful electro-magnet, and a current of 30 amperes was passed through for three hours. The current was then shut off, and the film shifted sideways for half an inch, and the action of the diamond without the magnetism was allowed to go on for another three hours. It was then developed, and both spots appeared about the same intensity.

25. The diamond crystal (17) in its brass box had a thin plate of clear mica put over the hole, and a sheet of lead over that. All was wrapped in sheet lead, and so kept for about six months. There was an extremely faint but hardly appreciable darkening of the mica at the position of the hole.

26. After the above experiment the diamond was kept in its brass box for two years, and then laid on a sensitive film and kept there for three hours. On developing a spot of action was seen, showing that the diamond was still radio-active. It was removed from its brass cell and examined in the dark on a blende screen. It gave plenty of scintillations easily visible without a lens. Experiments showed that it still gave out, along with α -rays, also β - and γ -rays (10, 19, 42, 43).

27. A small light-tight box was fitted as a camera. The arrangements were such that the image on the sensitive film was 1.5 times the size of the object. A photograph of the radio-active diamond (17) was taken by the light of its scintillations on the blende screen (17, 26, 30, 33), giving forty-eight hours' exposure. The three bunches of luminosity come from the corners of the crystal that are in contact with the screen. The photographic impres-

sion is certainly discontinuous, appearing granular—corresponding to the granular character of the screen. It appears that the different grains shine and continue to shine by their own residual phosphorescent light under the impact of the α -particles. In a further experiment the diamond was illuminated by the arc lamp, and a photograph was made of the diamond crystal *in situ* as well as of the screen. This gave a good image of the stone, and also of the granular surface of the screen.

28. It is certain that, in addition to α -rays, the diamond (17) gives off a considerable amount of other rays (10, 19, 26, 42, 43). This is shown by the early experiments, where photographic images with the diamond were obtained through one, two, three, and four sheets of aluminium foil—each 0.01 mm. thick.

29. The crystal of active diamond (17), with which most of these experiments have been made, was examined crystallographically by Dr. Tutton, who reported to me that the crystal is an apparent octahedron—but composed of two supplementary tetrahedra showing on three of the edges the usual grooves where the interpenetration of the tetrahedra is not complete.

30. Experiments show that exposure of a zinc-sulphide screen to the impact of electrons from the negative pole in a vacuum tube does not cause scintillations. It appears that only α -rays (positive atoms) produce this effect (11, 17, 26, 27, 33); it was therefore interesting to see if scintillations could be produced by bombarding a sulphide screen with a stream of positive atoms produced in a "Thompson" tube. An apparatus was fitted up having a zinc-sulphide screen to receive the positive discharge—but no effect of scintillation could be observed.

(To be continued).

IODOMETRIC EQUIVALENTS.

By A. J. G. SMOUT, A.I.C.

THE data given below has been found very useful for pasting up in table form in the laboratory where thiosulphate and iodine titrations form part of the routine:—

Value.		Value.	
Iodine	$\times 1.2465 = \text{Na}_2\text{S}_2\text{O}_3$	Log. =	0.0936
$\text{Na}_2\text{S}_2\text{O}_3$	$\times 0.8022 = \text{Iodine}$	"	1.9043
Iodine	$\times 0.2953 = \text{Arsenic}$	"	1.4703
Iodine	$\times 0.4722 = \text{Antimony}$	"	1.6741
Iodine	$\times 0.1263 = \text{Sulphur}$	"	1.1014
$\text{Na}_2\text{S}_2\text{O}_3$	$\times 0.2241 = \text{Chlorine}$	"	1.3504
$\text{Na}_2\text{S}_2\text{O}_3$	$\times 0.5051 = \text{Bromine}$	"	1.7034
$\text{Na}_2\text{S}_2\text{O}_3$	$\times 0.2747 = \text{Manganese dioxide}$	"	1.4389
$\text{Na}_2\text{S}_2\text{O}_3$	$\times 0.1292 = \text{Pot. chlorate}$	"	1.1113
$\text{Na}_2\text{S}_2\text{O}_3$	$\times 0.1461 = \text{Pot. perchlorate}$	"	1.1647
$\text{Na}_2\text{S}_2\text{O}_3$	$\times 0.1096 = \text{Chromium}$	"	1.0398
$\text{Na}_2\text{S}_2\text{O}_3$	$\times 0.4367 = \text{Lead}$	"	1.

TRADE WITH THE LEFT BANK OF THE RHINE.—The announcement on this subject issued by the Board of Trade on March 14 is hereby cancelled, and it is announced that it will no longer be necessary for re-exporters to obtain licences from the Export Licence Department before shipping to the territories on the left bank of the Rhine in the occupation of the Associated Governments goods other than those included in List A and B of prohibited exports.—*Board of Trade Journal*.

REVIVAL OF INDIGO.

IN addressing the Textile Institute, at Bradford, on February 27, on this subject, Prof. H. E. Armstrong took exception to the application of the adjective *natural* to indigo as redundant, also to the use of the expression *synthetic indigo*—as indigo never has been and never can be made artificially. Indigo is a mixed material, produced in a particular way from a plant, containing, in the case of well-made samples, about 70 per cent of the specific compound *indigotin*. This compound, not indigo, is the substance which is being manufactured and sold in an almost pure form. The term indigo should be used only in speaking of the natural product.

Indigo contains substances other than indigotin which have an influence in the dye vat, even if not actually dyestuffs. It has been the studied policy of the German manufacturers to disregard these associated materials as of no account; all but the old conservative school of dyers have fallen into the trap; these latter have always maintained that indigo has special qualities, which give it an advantage, in dyeing heavy shades, over manufactured indigotin pure and simple. Probably, in future, this difference will be one of determining influence in the industry.

In trials made with special care to contrast indigo with synthetic indigotin, in dyeing heavy shades on loose wool, the former has been found to have the advantage to a very marked extent. Hydrosulphite vats (1500 gallons) were set with equal quantities of indigo and of synthetic indigotin paste, each containing 20 per cent indigotin, and equal quantities of loose wool were dyed simultaneously in the two vats in lots of 50 lb. at a time. In the case of the first two or three dyeings deeper shades were obtained in the indigo vat. In consequence, the addition of paste before dyeing each lot of wool was gradually reduced, and it was eventually found that equal depths of shade were produced when the amount supplied each time was 8 lb. of synthetic paste and only $6\frac{1}{2}$ lb. indigo. Indigo produces a rather redder and brighter shade even when these proportions are used. The difference is being made the subject of systematic inquiry.

After considering the history of the introduction of synthetic indigotin and the position of indigo prior to the war, especially the great reduction in output of the natural product, Prof. Armstrong gave an account of the efforts made to improve the industry in India, in particular of late in Bihar, under the direction of Mr. W. A. Davis. It has been shown conclusively that a paste containing a standard proportion of indigotin, comparable with that in the synthetic paste on the market, is easily prepared, and that the only disadvantage it has arises from the presence of a certain proportion of insoluble matter. An organisation for the preparation of such paste has been established, and probably this material will be put on the market in competition with synthetic paste. Other forms, more easily transported, are in contemplation, however.

The process of manufacturing indigo has been much improved under Mr. Davis's direction—in particular the yield has been raised considerably by the recovery from the "seet" water of the finely divided, suspended indigo, which formerly ran to waste. This has been effected by adding Dhak gum.

The extraction process is being studied in every particular, especially on the bacterial side.

The crop has been a declining one of late years, owing to the diminished yield per acre, the occurrence of wilt disease, and the attack of the plant by an insect pest; also by reason of the difficulty of raising seed. A careful and extended survey of the results has led Mr. Davis to the conclusion that, at all events, the main cause of the decline is the depletion of the soils in available phosphate. Of late, even the Natal-Java plant has ceased to give a superior yield—the early success of this variety is shown to have been due to the fact that it is a very deep-rooted plant and was able to appropriate from the sub-soil the

phosphatic supplies beyond the reach of the Sumatran plant.

The future of the industry appears to be mainly contingent on the extent to which planters are able to apply phosphatic manures. Apart from the dyestuff it yields, the indigo plant is now of importance as a green manure; and as a leguminous crop it also has its definite, natural place in the rotation. It is clear that big crops can be obtained if proper agricultural conditions be secured, and that there will be no difficulty in raising seed. There is also reason to believe that improved varieties of the plant, giving an enhanced yield of indigo, will soon be produced. In short, improvements are foreshadowed in many directions, so that indigo may well recover its position and enter into effective competition with the artificially made somewhat imperfect substitute.—*Journal of the Society of Chemical Industry*, xxxviii., No. 7.

THE MANUFACTURE OF NEUTRAL SULPHATE OF AMMONIA. A NEW PROCESS.

MUCH interest has been shown at the present time in the matter of raising the standard of quality of the sulphate of ammonia generally supplied in this country. A strong movement is in being to persuade or compel manufacturers to eliminate the free acid which is a normal constituent of the sulphate ordinarily supplied. Such free acid is detrimental both to the transport and use of the salt. It rots the bags in which the salt is packed, and seriously impedes the agriculturalist in his efforts to secure an even distribution of the material in the soil.

It is not surprising that sulphate of ammonia which has been produced in the usual manner should contain free acid. The crystals of sulphate are deposited in a bath, which consists of more or less dilute sulphuric acid in association with a solution of sulphate of ammonia. As these crystals are removed from the bath they are, of necessity, surrounded by, and enveloped in, mother-liquor containing free sulphuric acid. Part of such acid drains away when the salt is allowed to rest; but a portion is left adhering to the crystals, and constitutes the free acid which is being objected to. In amount it varies from 0.3 to 1 per cent by weight of the salt; an average amount being about 0.5 per cent, where no special means are in use for its removal.

There are two ways by which this objectionable constituent may be got rid of. It may be eliminated, or it may be neutralised. For example, the salt may be washed with water, as in the following arrangement, for which a British patent was granted a year or two ago. There was an endless chain of perforated buckets dipping into the contents of the saturator, and raising therefrom the crystals of sulphate, which were met by a shower of water applied on the countercurrent principle—that is, the sulphate encountered progressively clearer or fresher water as it moved towards the discharge end of the conveyor. Thus the salt received a very effective washing, eliminating the free acid. But, unfortunately for the success of the process, the washing cannot be applied without at the same time some of the sulphate itself being dissolved. This is a very grave objection, and has prevented any extensive adoption of this method of washing the crystals of sulphate with water.

There are several patented methods for getting rid of the free acid by neutralising it. In one, the salt is exposed to vapourised ammonia, which is caused, by suitable means, to permeate the material. In others, a solid material containing ammonia in some weak combination is mechanically mixed with the sulphate which is to be made neutral, so that the free acid in the latter may combine with the ammonia that is presented to it. These methods of neutralising the free acid by means of added

ammonia, in one form or another, are quite efficient if properly carried out; but they are necessarily more or less expensive, seeing that the ingredient which is introduced into the sulphate must be brought into intimate contact with the latter, necessitating very careful mixture of the materials. Neutralised sulphate is said to be liable to become discoloured; and this is easily understood. For if an excess of ammonia be present in the material it will precipitate, as oxide, the trace of iron which exists in practically all commercial sulphuric acid.

We have now to describe a method which, by the introduction of a simple modification of the ordinary working arrangement, eliminates free acid from the resulting sulphate at practically no expense. This is the process devised by Mr. J. T. Sheard, the chief chemist to the Sheffield Gas Company, whose complete specification has just been accepted by the Patent Office. The process is based upon a realisation of the fact already alluded to, that every crystal of sulphate of ammonia, as it is removed or delivered from the saturator, is enveloped in a film of sulphuric acid, which in the ordinary course is too viscid to flow completely from off the surface of the salt. If, now, this film of acid can be diluted with water, so as sufficiently to reduce its viscosity, it will be enabled to flow away from the salt, leaving the latter practically neutral. In this process, therefore, the mass or magma of crystals enveloped in mother-liquor and acid, is surrounded by a fine mist or cloud of water, immediately it leaves the saturator, and before the mother-liquor has been allowed to drain away from it. The acid film enveloping the crystals of sulphate has a great avidity for water, which it absorbs, and is diluted by, while the salt is protected from meeting with the water, and so is not dissolved; for the water does not come directly into contact with the salt itself. The diluted mother-liquor, which drains away from the salt, carrying with it the free acid, flows back into the saturator. It might be thought that this would lead to too great weakening of the saturator bath; but this is not so. It is duly allowed for. In the ordinary way of working a supply of water, equal to 112 gallons per ton of sulphate made, must be provided, in some form or other, in order to reduce the strength of the acid employed—namely, 140° to 80° Twaddell, which is that generally considered the most useful. By the arrangement described, so much of the water as is necessary is used to dilute the acid on the surface of the salt removed from the saturator, before it enters the saturator itself.—*Gas Journal*, April 29, 1919.

THE COLOUR OF WATER.*

By WILDER D. BANCROFT, Ph.D.,
Professor of Physical Chemistry, Cornell University.

(Continued from p. 225).

"THERE is still another point which calls for attention. If the yellow colour of a liquid is due to the suspension of a certain number of solid or liquid particles, the colour should disappear as the particles sink; it should be ephemeral. If this were true, the suggested explanation of the different colours of natural waters would present a real difficulty; but this is not the case. I have allowed a turbid lime-water solution to stand for seventeen days in the observation tubes. At first no light came through, but after some time the lime began to precipitate in the tube, and the liquid became more and more green. At the end of twelve days the water was so clear that one could see through the tube a light pencil mark on a piece of paper. The colour of the water was green, nevertheless, and remained so. It was evident that I was dealing with a solution of lime in water without any real suspension of solid matter, and yet there was enough yellow left to form a

green with the blue of the water. Turbid waters containing bicarbonate of calcium or of barium in suspension show the same phenomenon, whence it follows that the resistance to the passage of light manifests itself also when light passes through saturated solutions where a precipitate is ready to form. This last might be called a nascent precipitate by analogy with the nascent clouds which Tyndall has taught us to recognise. To test this point experimentally, I have made at 18° a nearly saturated solution of pure calcium chloride containing no iron. In the observation tube this solution was a beautiful greenish-yellow. When diluted with water or when the thickness of the layer was decreased, the green became more marked. An almost saturated solution of pure magnesium chloride has shown a very pure golden yellow. A saturated solution of equally pure sodium chloride was wonderfully transparent and had a magnificent chrome-green colour. I have not examined solutions of other salts because of the difficulty of getting them really free from iron. I believe nevertheless that it is proved that the yellow colour produced by dissolving a salt depends less on the amount of salt dissolved than on the nearness of the solution to the crystallisation point. Small amounts of a slightly soluble salt will produce the same effect as large amounts of a more soluble substance. To test this directly, I boiled pure, blue, distilled water for some time in a glass flask. It is known that glass is slightly soluble in water. When the cooled water was poured into the observation tube, it proved to be completely opaque. After some hours a deep yellow light passed, and at the end of two days it became green and remained so. Its clearness was then very great, but the small amount of transparent material which had been taken from the glass was enough to colour it green.

"We can now show how the observed facts may be used to account for the colours of natural waters. We start with the assumption that a sufficiently thick layer of absolutely pure water has a beautiful blue colour. If small amounts of colourless salts are in true solution, the colour of the water will remain blue; but if the water contains greater or lesser amounts of a nascent precipitate the light passing through the water will be a more or less deep yellow. There may even come a point at which no light will pass and the liquid will appear opaque; in other words, black. The yellow light will necessarily blend with the blue of the water to form a series of tints which will vary with the amount of yellow from greenish-blue through bluish-green to green. If there is too much yellow, the blue will disappear and the water will be a brown yellow or even darker.

"Let us see now how these conditions may be realised in nature. The sparingly soluble substances in the natural waters, which may appear as nascent precipitates, are for the most part calcium carbonate, magnesium carbonate, silica, aluminium silicate or alumina. It is not necessary to consider the more soluble substances such as the chlorides and sulphates of sodium and magnesium because they do not occur in sufficient quantities to produce the effects in question. A blue water like the Lake of Geneva, or, better, like the Lake of Achen in the Tyrol, must have the calcareous matter more completely dissolved the more blue the water is. There must therefore be a sufficient amount of carbon dioxide to form calcium bicarbonate. A green water, on the other hand, like that of the Lake of Constance, must have the calcareous matter in a less perfect state of solution, which must be due to there being relatively less carbon dioxide in the water. It is interesting to note that these predictions are verified. In 1848 Sainte-Claire Deville analysed the green water of the Rhine at Strassburg and the blue waters of the Rhone at Geneva, determining also the dissolved carbon dioxide. (It is surprising that these two analyses are the only ones given in the chemical literature. Are there no others?). The data which interest us are given in Table IV. When referred to a constant quantity of calcium carbonate there is nearly relatively twice as much carbonic dioxide in the

* From the *Journal of the Franklin Institute* clxxxvii., No. 3.

waters of the Rhone as in those of the Rhine. The calcareous matter is therefore dissolved more completely in the former case and, as a matter of fact, the waters of the Rhone are blue.

"If it is true that, when other things are equal, a calcareous water is more blue the more completely the calcareous matter is dissolved, it ought to be possible to make a blue water green by bringing it in contact with lime-stone. The free carbon dioxide would then be converted completely into calcium bicarbonate. In the Lake of Achen the water is a deep blue out in the lake and a most beautiful chrome-green along the northern shore where the water is shallow and the bottom consists of lime-stone pebbles from which the waves grind off invisible particles of calcium carbonate, thus causing a change of colour. The greenish tones of shoals at sea and along the edges of lakes are probably due to the same thing. The sands of the sea contain fragments of crushed shells, and the lands along the shores of the lakes are usually sufficiently calcareous to saturate part of the carbon dioxide in the water.

TABLE IV.—(p.p.m.).

	Rhone.	Rhone.
Calcium carbonate ..	135.6	78.9
Free carbon dioxide ..	7.6	7.95

"So far we have considered only the calcareous matter; but silica and alumina can produce the same effect. A green water might contain no trace of calcareous matter, in which case the silica or alumina would have to produce the colour. Would a water containing alumina and silica give different tints and would it be possible to remove the alumina in any simple and natural way? The answer to this is easy. We know that clay or aluminium silicate forms a pseudo-solution in water though not soluble in the true sense of the word. The water of a river flowing over a fat, clayey mud, does not become completely clear on standing. Although the clay is not dissolved, it acts as though emulsified in the liquid. If one adds to the water a solution of a salt, such as sodium chloride, the aluminium silicate precipitates rapidly. This may be observed on an enormous scale at the mouths of large rivers. Their waters remain turbid even though the current has almost disappeared, so long as they do not mix with the seawater. When this happens, the mud settles rapidly, and this accounts for the formation of those deltas which are built up grain by grain and yet finally dam the river which formed them and force it to change its course. When the alumina precipitates the water becomes blue again. Reference has been made to the observations of Schleinitz on board the *Gazelle* as to the sudden changes in the colour of the sea. He noticed that there was an increase in the density of the water when the blue colour reappeared and he therefore concluded that the blue colour was due to the salt. The real explanation is that the salt precipitates the aluminium silicate, which had caused the green colour when present in suspension in the water.

"One other point may be raised. Is it not possible that the polarisation of the light observed by Hagenbach and by Soret in the Swiss lakes was due to the reflections which produce the yellow colour rather than to reflections producing the blue colour?"

While denying that suspended particles are the cause of the blue colour of water, Spring (*Bull. Acad. Roy. Belg.*, [3], 1886, xii., 814) recognises the important part which they play in the colour phenomena.

"One might think that the blue colour of water would be sufficient in itself to account for the blue colour of the Atlantic, the Mediterranean, and certain lakes; but this is not so. The action of water on the different components of white light varies very much. It absorbs the red strongly even in thin layers but it absorbs the other colours to some extent. If one were to examine the solar spectrum after sunlight has passed through an ever-increasing thickness of pure water, one would find the red, the orange, the yellow, and the green disappearing successively and

finally the blue when the thickness of the layer was sufficient. The light of the sun would therefore be absorbed completely in absolutely pure water if the water were deep enough. Such water would therefore appear as black as ink. Can such a depth of water be realised in nature? Some years ago Fol and Sarasin (*Comptes Rendus*, 1885, c., 991) made some new experiments to complete work begun by Fol and others, in which they showed that daylight does not penetrate more than two hundred metres into the waters of the Lake of Geneva even in calm weather and in the month of August. They proved this by lowering to different depths in the lake a special apparatus containing photographic dry plates with a rapid bromide emulsion made by our countryman Van Monckhoven. Those plates which were lowered 237—300 metres showed no effect of light when developed, whereas at 170 metres the illumination was apparently about equivalent to that on a clear but moonless night.

"Depths of more than two hundred metres are the rule not only in the ocean but also in most lakes. Consequently these deep waters, from which the light should never return, ought to appear absolutely black to us. Their surface might send back some reflected rays just as ink will; but the mass of the liquid ought not to appear coloured if it sends back no light. Along the shores and in the shallows the blue colour might show because the conditions would be more or less favourable for the daylight being reflected to the eye. The real phenomenon is quite different. The deepest waters are the bluest, and in the shallow waters the blue gives way to green or even to yellowish green and brown. How are we to account for this?"

"Tyndall has shown that no natural water is optically empty. Even after standing a long time the water of the Mediterranean and that of the Lake of Geneva scatters a beam of light. We therefore see the natural blue of certain seas and certain lakes because the daylight does not penetrate far enough into them to be absorbed completely. It encounters myriads of particles of foreign substances which reflect it in all directions like a multitude of microscopic mirrors. The effect to the observer is the same as though he were looking through a very thick layer. From this it follows that in a very deep and very clear lake containing relatively few suspended particles, a beam of light would penetrate further than into a more turbid water before all the rays would be reflected back. This clearer water would be a deeper blue and we find actually that the dark blue waters emit less light. It is also easy to explain the variations in the quality and intensity of these waters with sky changes or with varying agitation of the surface. . . .

"If the suspended particles are relatively numerous, a beam of incident light will not be reflected often in the water before melting the particle which will send it out. The blue will therefore not be saturated and will contain much white light. If the particles are few and far between, the beam will pass through a longer route in the water and the effect will be the same as though the observer were looking through a greater thickness. The blue will be more saturated and a deeper shade. In consequence of these multiple reflections the apparent illumination of the water does not necessarily come from a very great depth. The phenomenon is like that observed by all tourists in the mountains who have crossed freshly-fallen fields of snow consisting of the original small crystals which have not yet agglomerated to larger grains. Each hole made by sinking the point of the ice-axe in this snow is illuminated by the most beautiful blue light. This blue does not come from the depths of the ice or the snow, but is due to the fact that a ray of white light has been reflected a million times more or less from the surfaces of the little snow crystals before reaching the eye of the tourist. At each one of these reflections from a blue substance it has lost some of the reddish light and consequently appears more and more blue. This explains why the waters of some mountain torrents are a beautiful blue-

the intensity of which seems out of proportion to the depth of the water. The Ticino gives a series of illustrations of this between Airole and Belinzona. This explains why a light object, like an oar for instance, appears blue when plunged a little way into the water of a blue lake, even though the layer of water covering it is not itself sufficient to show the blue. The light reflected back by the object has not only traversed the slight depth between it and the surface, but comes also by reflection from the sides and is therefore blue.

"If the lateral distances are not sufficient, as is often the case near the shores of a lake or a sea, the phenomenon becomes complicated. The light coming from these points will necessarily be less saturated with blue even though the bottom is white. Since water absorbs most readily the least refrangible or red rays, and then the others less and less completely up to the blue rays, the less refrangible rays will not be cut off in a thin layer of water and the light will appear green. This is probably the reason that the waves of the blue sea appear green. One really sees them by light transmitted through a relatively thin layer."

In a later paper Spring (*Bull. Acad. Roy. Belg.* [3], 1896, xxxi., 94, 256) points out that an optically empty water may appear blue when seen from above if the temperature of the liquid is not homogeneous. A column of water unequally heated is equivalent to a light fog if the tube is short and to a dense black cloud if the tube is long enough. "The light is reflected and refracted from the layers of unequal density and is scattered irregularly in all directions as though the liquid contained infinitely small particles. In other words, such a medium does not behave like an optically empty one. This is important for the illumination of clear natural waters. A lake of pure water will appear blue if there are convection currents in it. The presence of solid particles is not absolutely necessary. If the convection currents are infrequent the lake will appear much darker, even though there has been no change in the chemical composition of the water. This is true experimentally. Forel (*Arch. Sci. Phys. Nat.*, 1877, lix.) points out that the soft water lakes are more transparent in winter than in summer. This is because in summer there is a greater difference between the temperatures at the surface and in the depths. In consequence of agitation due to many causes, the layers of water of different density do not remain stratified one above the other in a regular manner. They mix and convection currents are produced in all sorts of directions scattering the light every which way. Forel has observed that during the summer months it is absolutely impossible to see the bottom and to detect the ancient objects which one looks for in the ruins of the lacustrine cities at depths of 3-6 metres. In the winter the water is usually transparent enough to make the search profitable."

Special experiments showed that in a tube twenty-six metres long a difference of 0.57 between the water in the tube and the surrounding medium is enough to produce opacity. "This slight difference is quite within the order of temperature variations which must occur inevitably in the waters of lakes and seas. It makes us see that the tint cannot be the same in the zones exposed to the sun's rays and in the zones situated in the shadow of a cloud or a mountain. The water which receives the rays of the sun must appear more luminous not merely because of the greater amount of light which falls upon it but also because the solar energy makes the water less transparent than that in the shade. If the wind blows unevenly over the surface of the water, differences of the same order may be noted. The wind causes evaporation which lowers the temperature of the water, thus neutralising the convection currents due to the heating by the sun's rays, and making the water appear more transparent, or less illuminated. This accounts for the difference in tints to be noticed on the surface of lakes and seas, differences which indicate to some extent the direction of the wind."

(To be continued).

BOARD OF TRADE ANNOUNCEMENTS.

STANDARD FOR THE MEASUREMENT OF ELECTRICITY.

THE Board of Trade announce that the coils and instruments referred to in the Schedule to the Order in Council of January 10, 1910, which approved the several denominations of standards set out in that Schedule as denominations of standards for the measurement of electricity will on and after May 8, 1919, be deposited at the National Physical Laboratory, Teddington, Middlesex, instead of at the Board of Trade, Standardising Laboratory, 8, Richmond Terrace, Whitehall, London. All communications respecting Electrical Standards and instruments for test should on and after May 8, 1919, be sent to the Director of the National Physical Laboratory, Teddington, Middlesex.

SUPPLY OF GOODS TO THE RHINE TERRITORIES.

The Board of Trade have extended their General Licence authorising, on certain conditions, the supply of goods to the territories on the left bank of the Rhine in the occupation of the Armies of the Associated Governments, so as to cover, on the same conditions, the supply of goods to the occupied districts on the right bank. As regards both banks of the Rhine, applications should be made to the Export Licence Department, 4, Central Buildings, Westminster, S.W. 1, in respect of goods remaining on Section "A" or "B" of the Prohibited List which it is desired to despatch to the occupied areas (including Luxembourg). Goods on Section "C" of the Prohibited List do not now require a licence for export to the above-mentioned territory, provided in the case of shipment *via* Holland, they are first consigned to the Standard Bank of South Africa, Rotterdam. Goods on the "free" list may continue to be exported free of all restrictions. No import Permit from the Authorities in the occupied areas is now necessary, and the Notice on page 457 of the *Board of Trade Journal* of April 3, 1919, is therefore cancelled.

DYE INDUSTRY

The Board of Trade desire to give notice that, in accordance with the procedure laid down in the White Paper (No. Cd. 9194) setting out the scheme for affording State Assistance to the Dye Industry, the Trade and Licensing Committee have nominated the following gentlemen as the Licensing Sub-Committee to deal with all questions relating to the administration of the Prohibition of Import (No. 29) Proclamation, 1919, prohibiting the import of dyestuffs, &c., into the United Kingdom, viz., Mr. W. E. Kay (Calico Printers' Association, Ltd.); Dr. A. Ree (Association of British Chemical Manufacturers); Mr. J. Turner (British Dyes, Ltd.); Mr. Thorp Whitaker (Bradford Dyers Association, Ltd.). The Chairman of the Trade and Licensing Committee (Lord Colwyn) is also the Chairman of the Licensing Sub-Committee. The offices of the Licensing Sub-Committee are at Danlee Buildings, 53, Spring Gardens, Manchester, and any communications should be addressed to the Secretary (Mr. W. Graham) at that address.

IMPORT RESTRICTIONS.

The President of the Board of Trade, after duly considering the recommendations of the Consultative Council on Imports, has given the following further directions in regard to the Prohibitions of Import:—The restrictions on the importation of the following goods are to be removed:—

104. Bronze powder.
105. Waste or Scrap Rubber.
143. Glassware (including bottles and jars) other than scientific glass and glassware, machinery glass and glassware, machinery glass and glassware, optical glass and manufactures thereof, mineral lamp glasses, and miners' electric lamps are to be admitted at the rate of 50 per cent of 1913 imports.

Applications for special licences should be made as usual to the Department of Import Restrictions, 22, Carlisle Place, London, S.W. 1.

FLAX CONTROL BOARD.

The responsibility for the Flax Control Board has, by a decision of the Cabinet, been transferred to the Board of Trade as from April 1. The present members of the Board are being invited to continue to act, with the following amended terms of reference:—

"To promote and co-ordinate arrangements, whether by Government Departments or by private enterprise, for the supply and distribution of Flax, Flax Seed, and Flax manufactures for Government and Civilian purposes and to take such measures as may be necessary in regard thereto."

All communications with regard to the work of the Board should be addressed to Mr. P. Guedalla, Caxton House, Tothill Street, S.W. 1.

MOTOR SPIRIT LICENCES.

On and after May 17, 1919, Motor Spirit may be purchased without the production of a motor spirit licence.

Any holder of a full-duty or half-duty motor spirit licence who has not been supplied with the total amount of motor spirit authorised to be supplied by his licence may apply to the Petrol Control Department for an appropriate repayment of duty, and such application must be accompanied by the licence in respect of which repayment is claimed. Repayment will not be made in respect of loose vouchers.

Applications for repayment should be made as soon as possible after May 16, 1919, and addressed to the Petrol Control Department, 19, Berkeley Street, London, W. 1.

Free of duty motor spirit licences need not be returned to the Department.

PROCEEDINGS OF SOCIETIES.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, May 7, 1919.

Dr. SAMUEL RIDEAL, President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Andrew More, F.I.C.; John Haworth, F.I.C.; and H. T. Lee, M.Sc., A.I.C.

Certificates were read for the second time in favour of Messrs. Charles Frederick Lee Barber, A.I.C.; George Stanley Withers Marlow, B.Sc., F.I.C.; and Frederick William Read.

The following were elected members of the Society:—Messrs. Madanlal Jekisandas Gajjar and James Sorley, F.I.C.

The following papers were read:—

"The Analysis of Mercury and Zinc Cyanide and of Double Cyanide Gauze." By T. F. HARVEY, F.I.C., and F. MACKLEY.

Double cyanide gauze, so extensively used for field dressings during the war, is prepared by impregnating large rolls of gauze with a previously prepared paste containing about 50 per cent of mercury and zinc cyanide. Rapid methods of analysis used by the authors for the control of both paste and finished gauze are described.

"The Estimation of Small Quantities of Antimony." By W. BEAM, M.D., F.I.C., and G. A. FREAK, B.Sc., F.I.C.

The process is a modification of that proposed by Schidrowitz and Goldsbrough, and consists in depositing the metal on a strip of copper-foil as in the Reinsch test,

dissolving the antimony in a boiling alkaline permanganate solution, reduction with sulphur dioxide, and conversion of the antimony into colloidal trisulphide in the presence of gum. Colorimetric comparison is then made with solutions prepared from a standard potassium antimonyl tartrate solution.

"Studies in Steam Distillation." (Part VI.). By H. DROOP RICHMOND, F.I.C.

"The Detection of Cocaine, Heroine, and Veronal." By P. A. ELLIS RICHARDS, F.I.C.

ROYAL MICROSCOPICAL SOCIETY.

Ordinary Meeting, April 16, 1919.

Mr. J. E. BARNARD, President, in the Chair.

"Chemistry of Dendritic Growths in Paper." By JAMES STRACHAN.

The formation of these interesting and curious growths was formerly attributed to the oxidation of a particle of bronze or brass included in the sheet of paper during manufacture. Subsequent investigations have proved, however, that the chemical reactions producing these growths are more complex. The particle of bronze is attacked by chemical residues in the paper, chief among which is sulphate of aluminium, with the formation of soluble sulphate of copper. The latter creeps along the fibres in solution. The sulphate of copper is then reduced to insoluble black sulphide of copper, which constitutes the majority of recent dendrites in paper. This sulphide is further oxidised again to sulphate, and so by alternate oxidation and reduction insoluble copper compounds may be deposited along the fibres. The final action in old dendrites is oxidation resulting in the formation of basic copper sulphate. The chemistry of these growths is important in that they indicate, by secondary reactions, the nature of chemical actions taking place in the deterioration of paper during ageing, in which the cellulose is attacked by chemical residues from various sources. A new micro-chemical test for the detection of copper sulphide consists in the application to the dendrite of a solution containing the double cyanide of potassium and cadmium. The black copper sulphide dissolves, but is exactly replaced by a brilliant yellow pseudomorph of cadmium sulphide, forming a yellow dendrite. The principle of this mode of testing by replacement appears to be capable of further applications in micro-chemical manipulation.

"On Folliculina boltoni, S. Kent." By Dr. E. PENARD.

In spite of recent statements to the contrary, the genus *Folliculina* is undoubtedly represented in fresh water, and the vermiform bodies (described as *Lagynus ocellatus* by Daday) represent, as already suspected by several authors, though contradicted by others, a free-swimming form produced by a metamorphosis of the whole individual.

FARADAY SOCIETY AND RÖNTGEN SOCIETY. (JOINT MEETING).

A JOINT meeting of the Faraday Society and the Röntgen Society was held at the Rooms of the Royal Society, Burlington House, on Tuesday, April 29, for a discussion upon the "Examination of Materials by X-rays."

Sir ROBERT HADFIELD, F.R.S., opened the discussion, and also read a paper by himself and Messrs. S. A. Main, B.Sc., and J. Brooksbank, B.Sc., dealing with the absorption of X-rays by different kinds of steels and the examination of carbon electrodes used in steel making furnaces.

Prof. BRAGO gave a short address on the general principles governing the production of X-rays, and many other important papers were read, dealing chiefly with the

examination of metal castings and forgings with a view to revealing defects such as cracks, blow-holes, &c.

A paper by Major G. W. C. KAYE (ex-President of the Röntgen Society) attracted great attention. The subject was the examination of timber by X-rays, and many photographs were shown of the woodwork of aeroplane construction, and many unsuspected serious defects came to light. This method of examination has been of very great value during the war.

Other valuable papers were contributed, of which we hope to give an account in a later issue.

FIFTH NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES, CHICAGO.

DURING the week of September 23 to 27, inclusive, there will be given in the Coliseum and First Regiment Armory in Chicago, United States of America, the Fifth National Exposition of Chemical Industries. This is the fifth annual exposition, the four previous ones having been given at the Grand Central Palace in New York.

The Advisory Committee and the management of the Exposition extend to all the chemists of Great Britain, and manufacturers whose industries are based upon the chemical science as well as those interested in chemistry are invited to attend the Exposition. To visitors from this country they extend every facility and courtesy. They advise that there are in Chicago, a city which is a great metropolitan centre, and at the same time a great railroad centre, ample and comfortable as well as pleasant hotel accommodations.

The Advisory Committee of the Exposition is composed of:—Charles H. Herty, Chairman, Editor *Journal of Industrial and Engineering Chemistry*; Raymond F. Bacon, Director, Mellon Institute; L. H. Baekeland, Member Naval Consulting Board; W. D. Bancroft, President American Electrochemical Society; Henry B. Faber, Industrial Filtration Corporation; Ellwood Hendrick, President the Chemists' Club; Bernard C. Hesse, Chemist, General Chemical Co.; A. D. Little, President Arthur D. Little Inc.; Wm. H. Nicholas, President American Chemical Society; R. P. Perry, Vice-President the Barrett Co.; H. C. Parmelee, Editor *Chemical and Metallurgical Engineering*; G. W. Thompson, President American Institute of Chemical Engineers; T. B. Wagner, United States Food Products Corporation; M. C. Whitaker, President U.S. Industrial Chemical Co.; and Charles F. Roth and Fred W. Payne. There is also added a special Chicago committee consisting of L. V. Redman, W. D. Richardson, A. V. H. More, Carl S. Minor, F. W. Willard, and Wm. Hoskins; the managers are Charles F. Roth and Fred W. Payne, and the general office is at 417, South Dearborn Street, Chicago, Ills., U.S.A.

Speaking of the National Exposition of Chemical Industries they say that in the war preparedness of America the part performed by this Exposition was considerable. It was organised in the early days of the great war when America felt so greatly the need of chemicals in the form of dyes, medicinals, industrial chemicals and machinery, and equipment of all kinds. It took an active interest in the natural resources of the country, gathering together specimen exhibits of what the country contained, and brought to its halls the captains of industry and finance, out of the meeting of which with the raw materials and machinery that were shown came those great plants to manufacture the finished products that took so active a part in America's war programme as well as her domestic industries. Thus the Exposition has been the stimulus of the remarkable period of chemical development in America; the serious shortages in medicinals and dye-stuffs have been rapidly made good, textiles have been improved, food preservation put upon a better basis, the field of electro-chemistry expanded, the metallurgical industries enlarged, and the manufacture of machinery, apparatus,

and innumerable pieces of equipment, both for plant and laboratory, promoted and forwarded. The policy of the Exposition has been uniformly the serious task of enriching the country through the chemical industries, and has never sought popular favour by frivolous display or attractions.

America so well provided in her own industry holds and shows in this Exposition much of value and interest to British industry. With each succeeding year the practice has steadily grown among the exhibitors of withholding until Exposition week any new improvements or products developed during the year. All such recent developments made because of the exigencies of the war will have their public inception this September, and it is fair to predict that many things of exceptional interest will be shown; there is already an intimation from some sources that numerous new things will be released. The exhibitors' displays are always accompanied by the best technical men from the plants, who devote their entire time during the week to discussions of important technical details connected with the construction of plants, the installation and use of machinery on display, or the application and purposes of the numerous products without which the chemical and dependent industry would be at great disadvantage.

Of machinery, the displays consist of actual operating exhibits working upon materials and under conditions such as are found in any plant, and such operations on a large scale as cannot be shown are explained and carried before visitors by pictures in motion.

During the week of the Exposition there will be held, in the Exposition Buildings, annual meetings of the American Institute of Mining Engineers, the American Electrochemical Society, the American Ceramic Society, the Technical Association of the Pulp and Paper Industry, and the American Chemical Society is co-operating with the Exposition.

The previous Expositions have had an attendance of over a hundred thousand persons interested in the Exposition, with visitors coming from every point in the world. The present indication of the interest of scientific and business men in the Exposition, as evidenced by their interest in the society meetings just held, is expected to be a record-breaking attendance.

At this preliminary writing there are already 279 names on the register of exhibitors, nearly as great a number as at last year's Exposition.

While the programme of the Exposition is not yet announced there is every indication that it will be an exceedingly interesting and engaging one, and the whole Exposition as great a stimulus as during the early war period when its influence was so greatly needed.

NOTES.

NEW KAOLIN DEPOSITS.—New strata of kaolin have been discovered in the island of Börnholm. Temporary investigations indicate that the deposits are rich and that the quality is of the very best.—(*Berlingske T.*, Mar. 20.m., 1919).—*Technical Supplement.*

BENZOLE MOTOR SPIRIT.—In view of the increasing demand for benzole as a motor fuel the Commercial Motor Users Association (Inc.) has just issued a list of suppliers of benzole motor spirit throughout the country. The list, which has been compiled by Capt. F. G. Bristow, General Secretary of the Association, in conjunction with the National Benzole Association, is arranged in counties, and gives the name of the town, the address of the depot, and the hours during which benzole may be obtained. A copy of the list may be obtained, free of charge, on application to Capt. F. G. Bristow, General Secretary, Commercial Motor Users Association, 83, Pall Mall, London, S.W. 1.

THE WAR AND MOLYBDENUM.—The war had a marked effect in stimulating the production of molybdenum. On the outbreak of hostilities the price of molybdenite suddenly rose, and in a remarkable degree, the reason apparently being that Germany, aware of the impossibility of laying up enough tungsten, was buying molybdenite to take its place. During the war both England and France found themselves short of tungsten, and they, too, had recourse to molybdenum in the production of high-speed steels. The French used molybdenum in the breech-blocks of some of their field guns, but never, it appears, in shells, armour-plate, or gun-linings. Later in the war it was proposed to make armour-plate containing molybdenum, and contracts were entered into in America to produce such plate. Steel companies were parties to large contracts for molybdenum; but before the steel was actually put to use the war ended. One of the companies concerned used molybdenum, to the extent of less than 1 per cent, in making crank-shafts and connecting rods for Liberty motors.—(*Engineering and Mining Journal*, March 15, 1919).—*Technical Supplement*.

GERMAN IRON INDUSTRY WITHOUT "MINETTE" ORE.—The loss of the Briey Basin, with its immense deposits of rich iron ore, locally known as "Minette," is a staggering blow to the iron industry of West Germany. Germany has in recent years built up a great iron and steel industry, of which the principal centre is the Rhenish-Westphalian districts. It is affirmed that on that industry one-tenth of the population of Germany subsists. But the home production of ore has not kept pace with the output of finished iron, so that more than half of the requirements of the blast-furnaces has had to be imported, many foreign sources having been drawn upon. The ending of the war, so disastrous for Germany, has shaken this great industry to its foundations. The minette of Lorraine is henceforth unavailable. What this means to the industry of the Rhineland will be understood if we consider the fact that out of the 28.6 million tons of ore used in 1913, 21 million tons came to the works from Lorraine. France, which before the war was rich in iron ore, is now likely to become the richest in Europe, thanks in large part, the writer adds, to German intelligence and enterprise. For since 1870 the minette deposits have been brought into their present productive state under German management. German manufacturers must, therefore, set themselves to work the poorer ores of the country and carefully conserve all scrap.—(*Chemiker-Zeitung*, March 12, 1919).—*Technical Supplement*.

DYE-STUFFS.—DOMINION PRODUCTS.—In accordance with the policy of removing as far as possible restriction on the import of goods from the Dominions, the Trade and Licensing Committee have issued a general licence covering the importation into the United Kingdom of dye-stuffs, and other products covered by the Prohibition of Import (No. 29) Proclamation, which are of bona-fide Dominion origin. The Prohibition referred to was given in the issues of the *Journal* of February 27 and March 6.—*Board of Trade Journal*.

BENZOL FOR THE DYE INDUSTRY.—The Board of Trade desire to draw the attention of dye manufacturing firms to the fact that they are in a position to supply quantities of pure benzol for dye making purposes delivered ex storage tank at various centres at 1s. 9d. per gallon. As the supply is limited, it is desirable that inquiries, even if for forward delivery, should be made at once. All orders should be addressed to the Commissioner for Dyes, Board of Trade, 7, Whitehall Gardens, London, S.W. 1.—*Board of Trade Journal*.

WITHDRAWAL OF THE BLACK LISTS.—The Foreign Trade Department of the Foreign Office announce that the Allied and Associated Governments have decided that after midnight, April 28–29, all Black Lists of firms and persons which they have published or compiled shall be withdrawn, and that all disabilities attaching to trade and communication with firms or persons on such lists shall

cease to operate. The Allied and Associated Governments reserve the right to reintroduce all or any of such Black Lists should such action become necessary.—*Board of Trade Journal*.

BITES OF RABID DOGS.—The Local Government Board has issued a memorandum regarding the steps to be taken by persons who are bitten by dogs suspected to be rabid. The first part is especially interesting to chemists. The memorandum states:—The wound should be treated as soon as possible with undiluted carbolic acid, or with undiluted izar or similar disinfectant. The disinfectant should be allowed to come into contact with all parts of the wound, and should then be washed out with water or dilute disinfectant. If no disinfectant of the kind is available the wound should be thoroughly washed and irrigated with hot or cold water. Where it is possible to get the immediate services of a doctor the treatment should be placed in his hands. Persons bitten by stray dogs or by dogs exhibiting unusual behaviour should at once inform the police with a view to the necessary inquiries being made. By arrangement with the Board of Agriculture and Fisheries the names of all persons known to officers of that Department or to the police to have been bitten by dogs suspected of being rabid will be communicated at once to the medical officer of health of the district in which the bitten persons live. The Board of Agriculture have undertaken to advise the Local Government Board whether the symptoms in the dog are sufficiently suspicious to justify anti-rabic treatment before the confirmatory diagnosis is available, and this information will similarly be forwarded to the medical officer of health. In any case a definite decision for purposes of treatment will be available twenty-four to twenty-eight hours after the material for diagnosis from the dog has been received by the Board of Agriculture and Fisheries. When the medical officer of health is satisfied that anti-rabic treatment is essential, and has ascertained that the person bitten is prepared to begin the treatment, he should communicate with Dr. Dudgeon, Department of Pathology, St. Thomas's Hospital, Westminster Bridge, London.

DRY CELL.—French Patent No. 487,645 of A. Heinz describes a form of dry cell that may be stored permanently without deterioration. The positive electrode of manganese dioxide and graphite is enclosed in a tube of zinc, forming the negative electrode. The zinc tube is closed at its end by cardboard caps, and a hole is provided at one end to introduce the electrolyte just before the cell is put into service. The two electrodes are separated by a tube composed of paper mash boiled in a solution of carbonate of soda and then compressed. This tube is provided with a series of vertical slits.—(*Revue Générale de l'Electricité*, March 29, 1919).—*Technical Supplement*.

AN APPRECIATION.—When the United States came into the war, we promised, rather too rashly, to produce some 20,000 planes, perhaps in a year, but certainly within two years. We didn't do it. Great Britain made no promises, but what she did, though apparently little known, is far more than we promised to do. At the beginning of the war Great Britain's capacity for manufacturing airplanes was not greater than 100 per year. At the time the armistice was signed she was turning out planes at the rate of 800 a week! In other words, her production possibilities were demonstrated to be in excess of 40,000 planes a year! Think of that, and remember that it is not America, with her limitless resources of men and money and factory and raw material, but the British Isles, with their very much limited man-power, material resource, and steel industry, which not only built the planes but engined them. And then, as do all other fair-minded Americans who get the actual facts, take off your hat and bow in deep respect to a nation we of America are rather too apt to consider slow and old-fashioned in methods when it comes to factory production.—*Scientific American*.

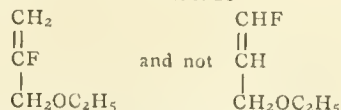
NOTES FROM FOREIGN SOURCES

Polymerisation of Formaldehyde by Alkalis.—C. Mannich.—It has already been shown that when alkalis act on formaldehyde either formic acid and methyl alcohol are formed, or else aldol condensation, resulting in the formation of "formoses," ensues. The author has found that another reaction may occur, namely, the formation of a polymer of formaldehyde, which separates as a white crystalline mass when moderately concentrated alkalis act at the ordinary temperature on 30 per cent formaldehyde solution. The analysis and the properties of the substance show that it is a polymeric formaldehyde. Auerbach and Barschall have already pointed out that when concentrated sulphuric acid acts on formaldehyde solutions four different polyoxymethylenes are obtained. The α - and β -modifications are soluble in sodium sulphite, while the γ and δ forms are insoluble. The α - and β -modifications are distinguished by their crystalline form and by their behaviour when boiled with water; only the α form is readily soluble in water. The polymerisation product obtained by the author so closely resembles α -polyoxymethylene that there can be no doubt that it is identical with it. —*Ber. Deut. Chem. Gesellschaft*, 1919, lii., 160.

New Method of Determining Oxalic Acid—Hugo Krause.—The method described by the author has the advantages of being very rapidly performed and requiring only simple apparatus. It can usually be carried out directly, since it is not affected by the presence of other organic or inorganic acids. The substance must be used in solid form. The method depends upon the conversion of oxalic acid into carbon monoxide, the volume of which is determined gasometrically. This reaction is well known to be brought about by the action of concentrated sulphuric acid, but it is not as generally known that acetic anhydride produces the same effect with great ease and rapidity, and quite quantitatively. When free oxalic acid is present an amount corresponding to about 0.1–0.3 gm. of oxalic acid is weighed out in a wide test-tube, fitted with inlet and outlet tubes and a small dropping funnel. Carbon dioxide is led in, and the outlet tube is connected with a Schiff's azotometer containing a 50 per cent caustic potash solution. After all the air has been expelled about 5 cc. of acetic anhydride is introduced through the funnel, and the test-tube is immersed in water at 50–60° which is rapidly heated until it boils gently. The volume of the carbon monoxide liberated is determined in the azotometer, and hence its weight is calculated. The method has to be modified somewhat if the oxalic acid is present as oxalate. If the oxalate is soluble in water it is simply dissolved in 15 per cent hydrochloric acid and then evaporated in the test-tube until a damp crystalline mass is obtained, which is treated as before. If insoluble oxalates are present they must be decomposed by using anhydride which contains sulphuric acid. In this last case the accuracy of the result is affected by the presence of malic acid and lactic acid. —*Ber. Deut. Chem. Gesellschaft*, 1919, lii., 426.

Bromfluorpropylethyl Ether and Fluorallylethyl Ether.—F. Svarts.—The substance used for the preparation of these two compounds was the ethyl ether of asymmetric dibromhydrine, obtained by the fixation of two atoms of bromine on allylethyl ether. It is best to work at a low temperature, and to dilute the allylethyl ether with an indifferent solvent. When mercurous fluoride acts on the ethyl ether an atom of fluorine displaces one of bromine. The temperature must be kept at 160–170° for a day, and then raised gradually to 200°, and the reaction is complete in two days. During the action hydrofluoric acid and hydrobromic acid are evolved, and a carbonaceous product is left after distillation. A small quantity of the difluorhydrine, $\text{CH}_2\text{F}-\text{CHF}-\text{CH}_2-\text{O}-\text{C}_2\text{H}_5$, is also formed. When bromfluorpropylethyl ether is subjected to the action of sodium methylate it loses a molecule of hydrobromic acid, and is transformed into fluorallylethyl ether. It is a very mobile liquid, having an odour resembling that of all the

allyl compounds. When oxidised it yields fluoracetic acid, and hence its formula must be—



which would give acetic acid. The formula of the bromfluorpropylethyl ether must therefore be $\text{CH}_2\text{Br}-\text{CHF}-\text{CH}_2-\text{O}-\text{C}_2\text{H}_5$. Fluorallylethyl ether readily combines with bromine, and the dibrom fluorpropylethyl ether obtained can be distilled without undergoing decomposition, which is an example of the effect fluorine has in rendering a compound stable, for the ethyl ether of dibromhydrine cannot be distilled under atmospheric pressure without undergoing decomposition. —*Bull. Soc. Chim. de France*, 1919, xxv., xxvi., 103.

Researches on Mercury Fulminate and some of its Impurities.—Paul Nicolardot and Jean Boudet.—Hyposulphite of ammonium and of sodium are both good solvents for mercury fulminate, and might both be used to test for impurities in the fulminate which are not soluble in them. The authors have systematically studied the action of the two hyposulphites, and of potassium cyanide upon the various impurities which might be present in the fulminate, such as mercurous or mercuric nitrate, mercurous or mercuric oxalate, and metallic mercury. The results show that hyposulphite is superior to cyanide, for the salts of mercury other than the fulminate are transformed by the hyposulphite into insoluble compounds, while under the action of cyanide they may go into solution and may be regarded as fulminate when the mercury is determined by electrolysis. Commercial mercury fulminate may contain a high proportion of impurities, and the authors regard Brounson's method of controlling the analysis of fulminate as very useful (*CHEMICAL NEWS*, 1904, lxxxix., 303). The following method of treating the residues in the manufacture of fulminate is simple and not expensive:—The fulminate contained in the residues is extracted by a solution of hyposulphite, the solution is separated off, acidified with a little sulphuric acid, and boiled. All the mercury then separates in the form of insoluble sulphide, which is filtered off. The mercury is recovered by distillation with lime. —*Bull. Soc. Chim. de France*, 1919, xxv., xxvi., 119.

Catalytic Dehydrogenation by Nickel in presence of Hydrogen.—Paul Sabatier and Georges Gaudion.—The hydrogenation of benzene hydrocarbons over nickel at a temperature of about 180° gives the corresponding cycloformic hydrocarbons. Thus, pinene yields the dihydride without any accessory reactions. But if the temperature is raised a different reaction occurs. If pinene and hydrogen are led over a column of liquid at about 350–360° a liquid is obtained which is hardly affected by sulphuric acid, but is energetically attacked by a sulpho-nitric mixture. This liquid consists of a mixture of benzene hydrocarbons (cymene and cymene) and a saturated hydrocarbon not attacked by the sulpho-nitric mixture. The density and absence of rotatory power indicate that it is a menthane and not pinene. Thus, hydrogenation and dehydrogenation occur simultaneously, but the presence of hydrogen is indispensable in order that the reaction may take place—without hydrogen a mixture of terpenes is obtained, arising from the isomerisation of pinene by heat, which is facilitated by the presence of nickel. Other compounds besides pinene undergo the same changes. Thus, limonene gives a little saturated hydrocarbon, but nearly all the product is a mixture of cymene and cumene. Camphene gives analogous results, and menthene reverts respectively to cymene and benzene. The same reaction has also been applied to oxygen compounds, and cyclohexanol, for example, has provided a regular yield of phenol. This method of dehydrogenation in presence of nickel can advantageously be applied to the production of benzols from terebentene, while the hydro-

generation' at lower temperatures (about 180–200°) gives only cyclones and formic hydrocarbons.—*Comptes Rendus*, 1919, clxviii., 670).

Utilisation of Glucose and Lævulose by the Higher Plants.—H. Colin.—It is known that the composition of the reducing sugar in the beetroot leaf differs in the lamina and the petiole. The ratio of dextrose to lævulose, often less than one in the leaf parenchyma, increases all along the medial vein and through the petiole. The same phenomenon is observed in chicory leaves and in most leaves with a fleshy petiole, which do not contain any carbohydrate except crystallisable sugar and the products of its hydrolysis; glucose is present in excess over lævulose in tissues which contain no chlorophyll. The etiolated leaves of beetroot, grown in absence of light, showed an excess of glucose, and also the subterranean parts of Jerusalem artichoke and the colourless leaves of chicory. It is simplest to suppose that the dextrose and lævulose migrate with unequal velocities and are utilised at unequal rates. The concentration of the hexoses in the cells is too low to allow of any appreciable difference in the viscosities, and consequently in the rates of diffusion. In these cases the dextrose is consumed less rapidly than the lævulose by the cells, and it is convenient to adopt the hypothesis of Brown and Morris according to which glucose undergoes combustion in the cell in preference to lævulose, which goes to build up the tissues. It is known that respiration is less energetic in the petiole than in the lamina and in etiolated than in green leaves.—*Comptes Rendus*, 1919, clxviii., 697.

Spontaneous Ignition of Mixtures of Air and Ether Vapour.—E. Allaire.—The author has studied the conditions governing the ignition of air and ether vapour, using a special apparatus by means of which the proportions of the two gases could be varied as desired. The apparatus consisted of a force pump driving air into a gas meter, the measured volume of air passing on into a tube in which it was mixed with ether vapour, obtained by the volatilisation of ether from a tube surrounded by a wire electrically heated. The pure ether was measured with a burette. Thus the proportion of ether at 0° and 760 mm. could easily be calculated if the temperature and pressure were known. The gaseous mixture was led into a U-tube, one limb of which was furnished with points like a Vigreux tube and having an opening through which a thermometer could be introduced into the bend. The whole tube was immersed in an oil-bath. Various catalysts, such as oxides of iron, copper, nickel, &c., were tried, but it was found that they had apparently no influence on the phenomenon, and the mixture ignited spontaneously at about 190°, when the amount of ether present was about 1 grm. per litre. The flame was pale blue, and visible only in the dark, and the products obtained were ethyl and methyl aldehydes and carbonic and acetic acids. No reaction took place before ignition occurred. A knowledge of this phenomenon explains the occurrence of accidents in factories and workshops in which ether vapour may spread accidentally in large quantities. It might be possible, by modifying the conditions of the experiment and by using tubes of greater diameter, to bring about ignition at lower temperatures.—*Comptes Rendus*, 1919, clxviii., 729.

Formation of Troostite at a low Temperature in Carbon Steels, and the Influence of the Temperature of Emersion in Interrupted Hardening.—M.M. Portevin and Garvin.—The authors have investigated cases of interrupted hardening, or hardening of limited duration, when the specimen was rapidly withdrawn from the hardening water at a temperature which is called the temperature of emersion. They have thus observed the formation of troostite at a much lower temperature than usual, but always with a marked characteristic recalcence. When the rate of hardening is decidedly greater than the critical rate, recalcence is observed at temperatures down to about 450°. If the rate of harden-

ing is lower than the critical rate, recalcence being already produced at a high temperature in the period of rapid cooling, troostite (or perlite) is always found, and the position of the temperature of emersion does not appreciably affect the structure or the hardness.—*Comptes Rendus*, 1919, clxviii., 731.

Spectral Structure of the J-Rays.—R. Ledoux-Lebard and A. Danvillier.—Barkla and Miss White have recently announced the discovery of the existence of a new series of X-rays, obtained by the absorption method with the lightest elements (C, O, and Al) and coming immediately above the K-rays in the scale of frequencies. It is interesting to study their spectral nature, which is possibly simpler than that of the K series, which comprises four monochromatic radiations. The only element which has the smallest atomic number ($N = 5$), and at the same time has physical properties which enable it to be used as anticathode, is boron, and moreover by extrapolation from the results of Barkla its J rays should fall in the absorption band of silver, so that the study of its rays by the photographic method is specially indicated. The authors have performed this investigation and find that the continuous spectra are very regular, the K discontinuities of bromine and silver being very clear. No ray of wave-length in the neighbourhood of $\lambda = 0.43$ A.U. nor even contained in the interval $1.0 < \lambda < 0.2$ A.U. could be detected, which is a remarkable fact for an element of atomic weight lower than those of the gases of the air. If the J-rays of boron are emitted with an appreciable intensity in proportion to the continuous spectrum they constitute a single ray which coincides with the K discontinuity of silver.—*Comptes Rendus*, 1919, clxviii., 608.

MEETINGS FOR THE WEEK.

Saturday, May 17.

Royal Institution, 3. "Caesar's Personal Character as seen in his Commentaries," by Dr. J. Wells.

Monday, May 19.

Institute of Metals, 8. (Ninth Annual May Lecture). "Radio-activity," by Prof. A. Soddy.

Royal Geographical Society, 5. "Uses of Geology in War," by Capt. W. B. R. King.

Tuesday, May 20.

Royal Institution, 3. "British Ethnology—The People of Ireland," by Prof. A. Keith.

Institution of Petroleum Technologists, 5.30. "The Chemist and Engineer in relation to the Petroleum Industry," by F. Mollwo Perkin and T. C. Palmer.

Wednesday, May 21.

Royal Society of Arts, 4.30. "Principles of Japanese Design," by Sir Francis Taylor Piggott.

Thursday, May 22.

Royal Society, 4. "Structure of Lysorophus as exposed by Serial Sections," by Prof. W. J. Sollas. "Preliminary Study of the Energy Expenditure and Food Requirements of Women Workers," by O. Rosenhain. "Report on the Metabolism of Female Munition Workers," by M. Greenwood, C. Hodson, and A. E. Tebb.

Institution of Electrical Engineers, 5.30. "Electrical Phenomena occurring in High Atmospheric Levels," by Dr. S. Chapman.

Royal Institution, 3. "Intensive Cultivation," by Prof. F. Keeble.

Friday, May 23.

Royal Institution, 5.30. "Hubert Hastings Parry—His Work and Place among British Composers," by Sir Alexander C. Mackenzie.

Saturday, May 24.

Royal Institution, 3. "Caesar as a General," by Dr. Wells.

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ON ACQUIRED RADIO-ACTIVITY.*

By Sir WILLIAM CROOKES, O.M., LL.D., D.Sc., &c.

(Concluded from p. 231.)

Action of Radium Emanation on Diamond and on other Bodies.

31. AFTER repeated observations on the action of radium on various substances, it was seen that diamond behaved differently to glass, quartz, and other materials, especially if the action of the radium had been continued for some length of time. The following experiments were made to see if definite light could be thrown upon this point. Some plates and crystals of pure quartz, lead glass, Faraday's boro-silicate lead glass, and three diamonds were selected—well cleaned, and exposed upon a sensitive film for twenty-four hours. On development it was seen that all were inactive, except in the case of two of the diamonds, but from these the action was so slight as to be only just visible upon the film. These objects were now laid upon a table of clean platinum gauze and enclosed in an airtight glass vessel, together with an open bottle containing pure radium bromide. They were allowed to remain exposed to radium emanation (33) for forty-eight hours; they were then removed from the chamber and laid upon a sensitive film for twenty-four hours. Upon development each object was found to be active and there was nothing to show that the three diamonds had acted differently to the quartz or glass. The objects were now all boiled in dilute nitric acid and thoroughly washed in clean water. They were placed on a film and allowed again to remain for twenty-four hours; on development it was seen that practically the whole of the "activity" had been removed—the two diamonds that originally were very slightly active had, perhaps, gained a little, but all the other objects had lost their temporary activity.

32. The experiments were still further extended. Two fragments of lead glass and one diamond crystal that had been buried in radium for over two years and had become deeply coloured, the diamond green and the lead glass brown, were removed from the radium and cleaned as far as possible with a dry brush. They were kept upon a film for five days. On development the photograph showed three equally dense black patches. The glass and diamond were now boiled in dilute nitric acid, thoroughly washed, laid upon a film, and kept there for eighteen hours. Upon development the pieces of glass were seen to have almost lost their activity—the diamond gave a dense black impression. The objects were now placed in a mixture of fuming nitric acid and potassium chlorate and kept just short of boiling-point for six hours, frequently removing the weakened solution and adding fresh acid and chlorate (3, 9, 12); they were then thoroughly cleaned, dried, and laid upon a film for eighteen hours. On development the glass blocks gave impressions slightly fainter than before, while the diamond still gave a dense black image almost as strong as before the treatment.

33. An examination with a zinc-sulphide screen showed that the diamond caused brilliant scintillations from its edges and corners and a few erratic scintillations could be detected round each of the fragments of glass (11, 17, 26, 27, 30). The net result of these experiments is to show that, although the well-known condensation of emanation (31) upon crystals and objects gives rise to

photographic markings of patterns as described in this research and in previous papers by Sir Ernest Rutherford ("Distribution of the Intensity of the Radiation from Radio-active Sources," *Phil. Mag.*, August, 1906) and other observers, this superficial activity can be easily and completely removed by washing in dilute acids. The diamond crystal that had been rendered active by immersion in dry radium bromide for some months in 1906 (17) and has been treated with acids, heated, and used in hundreds of experiments since—is apparently as active now as when it was removed from the radium, and still pours out streams of α -rays.

(These experiments are closely connected with those of Swinton, Colley, Ramsay, and others, who have shown that helium is driven into the glass walls of a vacuum tube even by the slower moving cathode rays. The high speed α -particles evidently are driven into the diamond, below the molecular surface.)

34. As in the case of diamond, a quartz glass dish after the action of radium retains its colour and activity, and continues to give off α , β , and γ rays. One-half had a film of aluminium, 0.035 mm. thick, interposed between the dish and the sensitive plate. Vessels of pure fused silica that have been much used for the crystallisation of radium salts become coloured a purplish tint, similar to that assumed by soda glass in similar circumstances. On heating such a coloured vessel with a spirit lamp to a temperature much below a red heat it suddenly phosphoresces a bluish colour and at a red heat becomes colourless.

35. A small equilateral prism was cut from a block of heavy glass (sp. gr. 3.87), polished on its three refracting faces, but left rough ground on the triangular top and bottom. It was put into a bottle and covered with dry crystals of radium bromide for fifteen hours. At the end of this time it was removed, well washed, and placed on a sensitive film, base downwards, for twenty-two hours. On development a strong action was apparent with overflow radiation along the sides and the continuation of the faces in triangular lines, as observed by Sir E. Rutherford.

36. One of the rough ground bases of the prism was now polished over the greater part of its surface, leaving a strip of glass along one edge in its original unpolished condition. This end was then laid on a sensitive film for thirty-six hours. On the polished portion of the surface there was absolutely no perceptible action on developing, while the part left unpolished was highly active—as in the first experiment with the prism.

37. The prism was now laid on a sensitive film on one of its polished faces for twenty-four hours. On development slight action was observed where the polished face touched the sensitive surface and a much stronger overflow action with continuation of the edges of the prism face in straight lines as mentioned above.

38. The same prism was taken, and a diagonal scratch made with a writing diamond across the same face that touched the film in the last experiment. It was laid with this face downwards on a sensitive film for twenty-four hours. On development the image showed action as before where the face touched the film, but the line of scratch where the surface of the glass had been abraded by the diamond was blank, showing no action whatever.

39. A triangular plate, about 1 mm. thick, was polished on its three edges, and kept in a bottle of solid radium bromide for sixty-eight hours, then laid on a sensitive film for four hours. There was very little action to be seen on development on the part where the face touched the film, but there was strong action radiating from the edges, with a continuation of the line of edge from each point. The plate was now cut into two equal parts, and the two halves, separated about a centimetre, were laid on a sensitive film and there kept for forty-eight hours. On developing, it was seen that the action of the flat surface was the same as before, but while the overflow action from the original corners was also the same, there was no action at all along the cut surface.

* A Paper read before the Royal Society. From the *Philosophical Transactions of the Royal Society*, ccxix., A, 521.

40. A glass tube that had contained 25 mgrms. of radium bromide was cut in half to remove the radium, and well washed and boiled in acids. It was of a dark blue colour. After being in a cabinet for many months the two halves were laid on a sensitive film in a line, the cut surfaces opposite each other and separated about 2 mm. After four hours' contact the film was developed, when the appearance presented that of a streaming brush discharge from the two ends of each half—the part where the tubes themselves rested having made no impression.

Superficial Action of Radium on Mica.

41. Radium bromide has been imported from the Continent in small ebonite boxes covered with a disc of mica. One of these discs was first well washed to remove any adhering grains of radium salt—it was then split into four flakes. The upper flake, of a strong brown colour, discharged the electroscope in three seconds. The next film, also showing brown discoloration, required 3.5 seconds. The third film, not discoloured at all, required twelve seconds, while the last film, which had been furthest from the radium, required eighteen seconds for discharge, showing that the greater part of the activity was near the surface and corresponded with the coloration.

Action of X-rays on Diamond.

42. Experiments were instituted to ascertain how X-rays affected the diamond. A tray full of crystals of diamonds was exposed to X-rays from a hard tube, covered in card and velvet so as to prevent interference from the luminosity of the glass. Most of the stones became luminous—but in different degrees. Two stones specially were

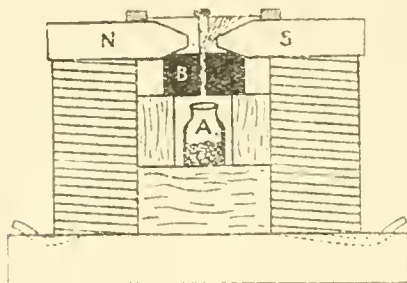


FIG. 1.

noticed. One large stone shone very brightly, with a blue tint, the other, smaller, was only just luminous. A sheet of aluminium, 3.2 mm. thick, was now interposed in the path of the X-rays, when the phosphorescence of the large bright stone was considerably reduced, while that of the small faint stone was not diminished at all.

Action of β rays on Diamond.

These two diamonds were subjected to the action of solid radium bromide, and the intensity of the phosphorescence thereby induced was seen to be of the same character as that caused by the X-rays. An extension of the experiment with radium, described in the next paragraph, showed that the effect of phosphorescence was mostly due to the β -rays (10, 19, 26).

43. An apparatus (Fig. 1) was fitted so that the active rays from a bottle of radium bromide (A) should pass through a tube drilled through a lead block (B), and allowed to pass upwards on a diamond (C) supported on a plate of aluminium, 0.02 mm. thick. This was arranged between the poles of a powerful electro-magnet, so that the active rays from the radium should pass through the hole and act on the diamond when the magnetism was off, and be deflected from it when the magnetism was on.

A screen of barium platinocyanide put over the hole in the lead block showed a circular spot of phosphorescence. This luminosity vanished when magnetism was turned on, and reappeared when it was turned off, showing that the luminosity on the screen was chiefly due to the β -rays (10, 19, 26). The two large and small diamonds used in the last experiment were put side by side on the aluminium, and the support so arranged that it could be moved sideways to put either stone over or away from the hole in the lead block. It was easy to see by small movements of the support that, as in the case of the X-rays, the large stone was much more phosphorescent than the smaller stone. There was considerable residual luminosity, each of the stones continuing to glow with its relative intensity when effectually removed from the radium. Having found the position of maximum brightness for the large stone when over the radium, the current was turned on, so as to deflect the β -rays. At once the glow declined, and the residual phosphorescence faded. On taking the current off, so as to allow the β -rays again to come into action, the brilliancy increased again. There was no doubt as to the action, although the undeflected γ -rays and the residual luminosity tended to obscure the observations.

44. The results described in this paper may be summarised as follows:—Various objects, diamond, ruby, garnet, quartz, gold, platinum, &c., also the phosphorescent substances yttria, calcium sulphide, zinc blende, and barium platinocyanide, are bombarded in a high vacuum by cathode rays, and in no case can any permanent activity be recognised either by photographic or electrical means (1, 2, 3, 4, 5, 6, 7).

Exposure to radium emanation confers temporary radio-activity on all bodies that have been tried; apparently due to the condensation of the emanation on the surface. This transient activity can be completely removed by washing in dilute acids (31).

Many substances become coloured by direct exposure to radium, the colour depending on the substance. Diamonds take a full sage-green tint, the depth depending on the time of exposure to the radium (33).

In addition to change of colour diamond also becomes persistently radio-active, continuously giving off α -, β -, and γ -rays. The acquired colour and activity withstand the action of powerful chemical agents, and continue for years with apparently undiminished activity (12, 31, 32).

Removing the surface by mechanical means removes both colour and radio-activity (13, 16, 35, 37, 41).

The appearance of an auto-radiograph made by placing an active diamond crystal on a sensitive photographic plate, and the visual examination of its "scintillation" luminosity, suggest that there is a special discharge of energy from the corners and points of the crystal (18, 21, 23, 27, 33).

THE ANALYSIS OF PRUNE KERNELS.

By LUCIA FORDYCE and D. M. TORRANCE.

IN the work we use 50 grms. of kernels. These were crushed, placed in a 250 cc. flask, connected with an inverted condenser, and ether was added. They were heated on the water-bath for more than sixty hours, when all the oil was extracted. The ether was then removed by distillation.

To get rid of the last traces of ether the residue, mostly oil, was placed in an open beaker and heated on the water-bath for two or three hours. We obtained 21 grms., or 42 per cent of oil.

On cooling the oils two kinds were found to be present. They were placed in a freezing mixture, and at minus 5° one of them solidified. The other oil was drawn off by means of a pipette and each was weighed. The oil which solidified weighed 7.0122 grms., and had a specific

gravity of 0.9055, and the other which remained liquid weighed 14 grms. and its specific gravity was 0.9119.

To ascertain if the oils were volatile 2 cc. were left standing in the open air for forty hours. There seemed to be no loss in weight.

The saponification equivalent was found by treating a portion of the oils with 30 cc. of normal caustic potash solution in absolute alcohol. This was heated on the water-bath for twenty hours with an inverted condenser, when saponification seemed to be complete. It was then titrated with normal hydrochloric acid.

The portion that solidified at minus 5° resembled palm-nut oil, and had a saponification equivalent of 239.8. The saponification equivalent of palm-nut oil is 241 and its specific gravity is 0.9055.

The saponification equivalent of the liquid portion of the oil was found to be 207.4. It has the characteristics of cocoa-nut oil, whose saponification equivalent is 209 and its specific gravity is 0.874.

When 50 grms. of the kernels were treated with alcohol instead of ether a very small quantity of solid oil separated out, but the amount was too small to investigate further.

The kernels remaining after the ether extraction were dried in the air for ten hours, and then at a temperature of 100° for fifteen hours; the dried residue weighed 23 grms.

The Gunning method was employed for the estimation of nitrogen. We obtained 2.47 per cent of nitrogen from the original kernels and 2.21 per cent from the residue after the oil was removed.

We extracted the sugar with Maxwell's apparatus (CHEMICAL NEWS, cxvii., 122), using water as the solvent. The kernels were boiled for 250 hours, when no further trace of sugar could be detected with Fehling's solution. We obtained 37.42 per cent of sugar. By treating a solution of the sugar with sodium acetate and phenyl hydrazine hydrochloride we could detect the presence of fructose and glucose, with a possible small amount of cane-sugar.

Cornell College, April 22, 1919.

NOTES ON THE DETERMINATION OF CARBON IN STEEL.

By L. JOSLIN ROGERS (University of Toronto).

THE development of a new absorbent mixture for carbon dioxide, soda asbestos, has so simplified the apparatus used in carbon determinations that it is quite evident that this material will soon replace all others for this type of work.

Until recently there were practically two types of bulbs, those using potassium hydroxide solution and those requiring soda lime. The great drawback to the first class of bulbs was the inability to permit a flow of gas at a rate sufficient to allow of rapid work required in present-day practice. The introduction of the Fleming tower made possible the seven minute carbon determination. This rapidity led to the application of this method to supplant the inaccurate colour carbon in the "snap test" on a heat of steel.

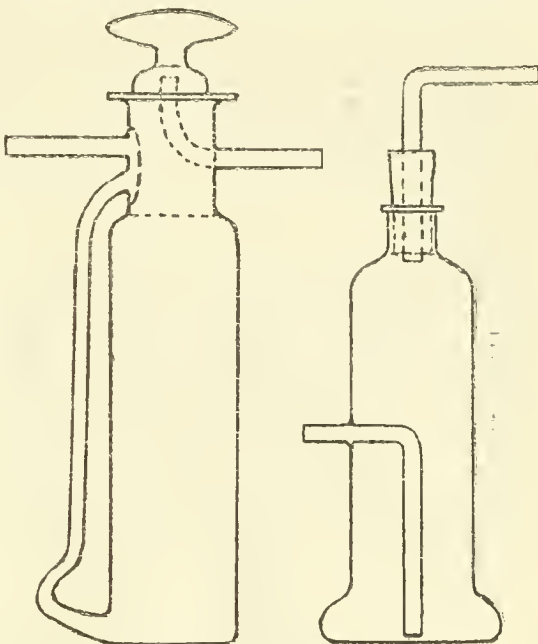
The Fleming tower, which has been for the past five years coming steadily forward on account of its marked superiority over the wet towers, has in its turn several features which require most careful attention in order to secure exact results. These are as follows:—The soda lime used must be of the proper fineness, and its moisture content must be about 15 per cent. This excess of moisture rapidly consumes the pentoxide in the top chamber, which will accordingly require frequent renewal. Again both the soda lime and the pentoxide must be carefully watched for fissures which will permit the gas to pass through without absorption. The weight of the bulb is

such that it requires a 200 grm. balance to give satisfactory results, and naturally this leads to slow weighings. In spite of all these points the tower has steadily gained place, due to its increased functions over the wet towers.

The new absorbent, soda asbestos, eliminates almost every undesirable feature of any combination yet placed in the hands of the chemist for the determination of CO₂ gravimetrically.

The absorbent is sold in granular form about 8 to 10 mesh. It serves as its own drier, no pentoxide or calcium chloride being required. It will absorb nearly 10 per cent of its weight of carbon dioxide, and can be used while the gas is flowing from 250-300 cc. per minute. The containing tower has a relatively small area and weighs loaded about 100 grms.

The Midvale bulb modified according to Stetser and Norton is a very simple and inexpensive apparatus, designed particularly for use with soda asbestos. The Nesbitt bulb, designed originally for soda lime and pentoxide, serves as an ideal apparatus. This latter bulb



was rather a failure for the original purpose intended, since it had only a layer of asbestos between the pentoxide and soda lime, and the top portion of the latter rapidly dried out and became useless. However, this bulb leaves almost nothing to be desired further when used with soda asbestos. One slight turn of the single stopper as seen in the diagram shuts off the bulb entirely from the air. There are no rubber portions to catch foreign material as dust, &c., and the exposed glass area is relatively small. The stopper is large, permitting easy filling. The Nesbitt bulb is used with the gas flowing in at the top, and has therefore only a packing of glass-wool over the aperture at the bottom. Since soda asbestos is of coarse granular structure, there is no loss of fine particles and the tower never fissures. It is a very satisfactory material also for filling the drying arm in either a Johnson or Vanier bulb.

Another feature which makes the use of either the Fleming or soda asbestos bulb desirable is that both towers will permit of a flow of gas fast enough that a full factor weight of steel may be burned to a fusion without altering the rate. This use of a full factor weight is very desirable from several standpoints. The weight in mgrams.

between successive weighings gives the carbon content in points. A system of weighing and recording as given in the tabular scheme allows the operator to check the gross increase in tower weight with the total individual increases; thus mathematical errors are detected. These errors on the balance constitute a very high percentage of all errors in carbon determinations.

By the use of a factor weight of steel of the proper fineness a heat is developed which gives a complete fusion of the steel, and a consequently accurate result. Many chemists desire to burn fine thin ribbon like drillings, believing that they give better results. This is not the case, however, since drillings which are fine and ribbon-like occupy the whole length of the boat, and, indeed, it is sometimes difficult to place a factor weight of them on an ordinary boat. Spilling frequently occurs. If there are any coarse particles whatever, these will be left unburned because of the fact that the steel is not in small enough area to permit of development of sufficient heat to fuse the whole mass down.

The idea formerly held that fused steel cinder contained included carbon has been practically discarded by all. The steel should be fused as completely as though it had been burned with red lead. Caution is necessary, however, that the bedding material in the boats should not contain silica. A silicious bedding, especially where a small amount is placed on top of the steel to prevent "spraying" will invariably cause low results.

When using sufficient heat and steel to effect a complete fusion the usual clay boats will give but very little satisfaction, since they will cut through in sometimes only a few determinations. This adds materially to the cost per determination.

Nickel boats which are among the most durable were for a long time unsuitable because of the high carbon content. This in some material runs as high as 0.20 per cent. Recently, however, sheet nickel 1 millimetre thick has been secured which has a very low carbon content, and after short treatment in a muffle will give up no further carbon whatever. These are the most suitable and durable boats for combustion of steel where a fusion is desired.

SAMPLE OF RECORD SHEET.

Tabular Record for Checking Results when using Factor Weight.

Sample No.	Time.	Tower wt.	Diff.	Remarks.
			Per cent	
Blank.		101.6352	carbon.	
No. 1.	10.10	.6844	.0492	
No. 2.		.7219	.0375	
No. 3.		.7665	.0416	
		11313 A	1513 B	

(A) is the difference between weight of tower at initial point and after third determination.

(B) is sum of first three determinations.

—*Canadian Chemical Journal*, April, 1919.

COLLOIDAL FUELS.

COMPOSITES OF OIL, TAR, AND CARBON.

THE Executive Committee of the Submarine Defence Association, New York, have authorised the publication of a statement concerning new colloidal fuels developed under their auspices since the United States entered the war, and now fully tested and demonstrated. The author of the report is Mr. Lindon W. Bates (the Chairman of the Engineering Committee of the Association), in whose hand rests the commercial introduction of colloidal fuel, and who has had personal direction of its development. In making an oil and coal composite, an insuperable diffi-

culty heretofore has been the persistent settling-out or sedimentation of the heavy coal and tar particles. This destroyed the value and utility of all mechanical mixtures.

To-day, the report states, it is possible to suspend for months in oil 30 to 40 per cent of coal, pulverised so that about 95 per cent passes through a 200-mesh screen, assisting the suspension with a special fixateur. It is possible to combine in a stable liquid fuel about 45 per cent of oil, 20 per cent of tar, and 35 per cent of pulverised coal, thereby replacing over one-half of the oil, securing equal or greater heat values per barrel, and saving considerable cost. Pulverised coal burned alone cannot in many cases replace oil. Especially is this true on ship-board. Radical changes in oil-burning installations become necessary; and its storage requires too much space, and in this way limits the cruising radius of war vessels.

Pulverised coal can be successfully held in suspension, so that the colloidal liquid flows freely through the pipes, preheaters, and burners of ships, and power, heating, and industrial plants equipped to burn fuel oil. Months after mixing, the composites show little or no deposit. A fixateur, which comprises about 1 per cent or 20 lbs. per ton, acts to stabilise the particles of pulverised coal dispersed in the oil. In colloidal fuel, every solid particle has its film of liquid hydrocarbon and a protective and peptising colloid, itself combustible. The particles are in three classes as to dimensions—coarse, colloid, and molecular. By coarse is meant the fineness of fifty million particles per cubic inch. The fixateur and fixated oils are readily made, and may be shipped anywhere. The manufacture or distribution of the new fuels incorporating solid carbons in fixated oils involves no doubtful process or industrial problem. On burning the combustion is so complete that, with fair coal, there is left no slag and very little ash; what there is being light as pumice and granular as sand.

It is the property of colloidal fuel that, without loss of efficiency per unit volume or change of oil storage or burning equipment, it makes possible the conservation of at least 25 per cent of the fuel oil now burned, or, conversely, with the oils now available it increases by 50 per cent the world supply of fuel that is liquid. A number of new fuels have been realised, each with varying percentages of oil and solid carbon. One useful composite, in the range of ordinary temperatures, is composed of about one-half coal and one-half oil. Another unctuous semi-liquid is nearly three-fourths coal and one-fourth oil. All the fuel pastes are mobile to sustained and easily applied pressure, and may thus be pumped, fed, and atomised in the combustion chamber. These semi-fluid composites will constitute the most compact and safest fuel for domestic and industrial use; and they will largely eliminate the smoke and ash nuisances of cities.

As an example of conservation to be effected through the new colloidal fuel, the report gives an estimate of what would result by its substitution for the 2,900,000 barrels of oil now consumed yearly in the power plants of New England. By displacing only 25 per cent of the oil with pulverised coal, a saving of 675,000 barrels would be secured. Estimates of the cost of this new fuel indicate a valuable reduction in the fuel expenses of New England power plants. Moreover, in New England, graphitic anthracites, gas house coke and tar, and charcoal can be used effectively. Thus there may be a marked saving of transport—30 per cent as to oil, and 30 per cent as to coal. On the other hand, the 2,900,000 barrels brought to New England, when employed in colloidal fuel, can do the work of nearly 4,000,000 barrels, with the marked economies and advantages inherent to producing and applying heat with liquid as against solid fuel. Each locality may have its special composite, containing the cheapest available coal, oil, and other ingredients.

A demonstration test unit, to manufacture and use colloidal fuel on land, is installed at Brooklyn; and it is now to be tested at several steel-making plants. The

largest field of use and oil conservation is in furnace work—direct fired, reverberatory, regenerative, and crucible furnaces; for brick-kilns, for air, annealing, bolt-heading, blacksmithing, brass melting, billet heating, forging, rivet heating, and open-hearth furnaces now fitted for oil. About 70 per cent of the oil they now use will do the present duty of 100 per cent, and do it more cheaply. A certain steel plant uses 3000 barrels of oil daily, and will soon require 4500 barrels. But the 3000 barrels of oil with coal incorporated and used in colloidal fuel will be ample for full output, saving about 500,000 barrels per annum, with less cost, and with great conservation of actual oil and oil transport. There are legions of liquid fuel users large and small. As a corollary of these developments there will be very many more.

A further research was started by Mr. Baker in response to a suggestion from the Admiralty to try blending petroleum oils and coal-tars, and see if it was practicable to stabilise the mixture so that free coke and asphaltic substances would not settle-out, but would produce a stable liquid fuel that could be shipped, piped, and stored. The quest was well worth while, because could it succeed one might so create annually in America and in England up to 20,000,000 barrels of superior liquid fuel, without an increase in oil-well production. Success is now confirmed. Thus countries without oil may themselves produce over one-half of the substances to make liquid fuel; and as the gas-house and coke-oven tars are usually cheaper than fuel oil, they will average-down the cost of oil in the composite.

To produce colloidal fuels there are required:—

1. Certain processes modified, if need be, to suit the blend or grade desired.

2. Certain fixateurs. Their offices are primarily to stabilise synthetic fuels whose separate elements are of different specific gravities and characters, so that the finished products have each a homogeneous and definite nature. Regarding the nature of the fixateurs and special incorporation and treatment process, it will suffice to say that the fixateurs and treatments produce a state in which the settling force of gravity, operating upon the particles somewhat according to Stokes' Law, is overcome by peptisation, absorption, Brownian movement, electrical factors, and other chemical and physical phenomena—including such as obtain in colloids of metals, only that in the new case many of the particles are above colloidal size.

3. Certain substances incorporated during the main process or when forming the "fixateur" which is itself incorporated. Their offices and properties are to effect chemically, or physically, or electrically, the characteristics of the components of colloidal fuels, either alone or in association with liquid or other combustible or non-combustible substances. They have properties in particular reference to—Suspending and dispersing solid particles of coarse, colloidal, and molecular dimensions (coarse being used in a relative sense), or fluid sludge or asphaltic ooze, in a liquid or mobile gel or paste; dissolving and peptising; establishing the desired viscosity, melting or fusing point, the chilling range or the desired flash-point; fluxing; enriching with combustible elements; dehydrating or hydrating; affecting the ash content and the sulphur content on combustion, catalysing, or promoting the miscibility of two or more liquids; drying and inoculation. Some of these substances may remain in the colloidal fuel product in whole or in part, or, having performed their set duty, may be mostly distilled off and recovered and used again and again.

One of the advantages stated by Mr. Lucius H. Beers (the Chairman of the Submarine Defence Association) in a letter accompanying Mr. Bates's report, is that in making colloidal fuel great deposits of low-grade coal, which have been largely unavailable, as well as vast quantities of lignites, brown coals, and wasted dust, are added to the world's fuel supplies.—*Gas Journal*, cxlvi., No. 2919, April 22, 1919.

GALLIUM.*

By L. M. DENNIS and J. ALLINGTON BRIDGMAN.

THIS article deals with the spectroscopic detection of gallium, indium, and zinc; the purification of gallium; the determination of gallium, and of gallium, indium, zinc; and aluminium in the presence of one another; and the preparation and properties of two new salts of gallium, and the properties of some salts that had previously been prepared.

Material.

The crude material employed in this investigation consisted of about 35 grms. of an alloy consisting chiefly of gallium and indium, which was generously presented to us by Mr. Kurt Stock, Superintendent of the Bartlesville Zinc Company, Bartlesville, Oklahoma. (For descriptions of the separation of this alloy from spelter, see Hillebrand and Sherer, *Journ. Ind. Eng. Chem.*, 1916, viii., 225; Browning and Uhler, *Am. Journ. Sci.*, 1916, xli., 351). It would have been of interest to determine the percentages of gallium and indium in the alloy before undertaking the preparation of pure gallium from the material, but this was not possible because at the beginning of the investigation no method of accurately determining gallium and indium in the presence of each other was known. Results that were obtained during the process of purification of the gallium indicated, however, that the alloy contained not over 8 per cent of indium, somewhat less than 1 per cent of zinc, and traces of cadmium and copper.

Spectroscopic Detection of Gallium, Indium, and Zinc.

Before taking up the study of the purification of gallium it was necessary to develop some method by means of which the purity of the various preparations of gallium might be ascertained as the work proceeded. The two elements whose presence in the gallium was chiefly to be expected were indium and zinc, because they are associated in largest amount with the gallium in the alloy. The spectroscopic examination of the material naturally suggested itself as the best method to employ, and inasmuch as no statements have hitherto appeared in the literature as to the delicacy of the spectroscopic detection of these three elements in the presence of one another, this subject was first investigated. Two types of spectra were studied: spark spectra, which were observed with the eye, and arc spectra, which were photographed.

The Detection of Gallium and Indium by means of their Spark Spectra.

There were needed for these tests a solution of a salt of gallium that was substantially free from indium, and a solution of a salt of indium free from gallium.

The first of these was prepared by dissolving a portion of the original alloy in aqua regia, and freeing the solution from indium by adding an excess of potassium hydroxide and boiling the solution (Lecoq de Boisbaudran, *Comptes Rendus*, 1882, xcv., 410). The precipitated indium hydroxide, which, as we later ascertained, carries with it some gallium hydroxide, was removed by filtration, and metallic gallium was separated from the alkaline filtrate by electrolysis. The metal was dissolved in aqua regia, ammonium hydroxide was added. The precipitated gallium hydroxide was washed, dried, and ignited, and yielded 1.0819 gm. of gallium oxide. This product was dissolved in 10 cc. of concentrated hydrochloric acid, and the resulting solution was diluted to 25 cc. This solution of gallium chloride, which contained 0.0322 gm. of gallium per cc., was used in the spectroscopic tests.

* This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by J. Allington Bridgman in partial fulfilment of the requirements for the degree of Doctor of Philosophy. From the *Journal of the American Chemical Society*, xli., No. 10.

A solution of indium chloride free from gallium was prepared by dissolving in water a portion (0.7988 gm.) of the pure indium chloride prepared by F. C. Mathers in this laboratory in connection with his work on the atomic weight of indium (*Journ. Am. Chem. Soc.*, 1907, xxix., 485). The solution was diluted to 25 cc., and hence contained 0.0166 gm. of indium per cc.

The apparatus that was employed for the observation of the spark spectra consisted of a Krüss spectroscopic induction coil capable of giving a spark about 1 inch in length, and small glass cups for holding the solutions. The cup was made by fusing a piece of platinum wire into the end of a piece of glass tubing 7 mm. in diameter, and then cutting off the tube about 6 mm. from the closed end. Such a cup holds about three drops of liquid.

Detection of Gallium.—Twenty cc. of hydrochloric acid was added to 80 cc. of water. Into this diluted acid one drop of the solution of gallium chloride (1 cc. = 0.0322 gm. Ga) was introduced. Three drops of this very dilute solution of gallium chloride were then brought into one of the glass spark cups, and the spark spectrum of the solution was examined. The best results were obtained with a short spark and a heavy current through the primarity of the coil. A second drop of the solution of gallium chloride was then added to the diluted hydrochloric acid, and a sample of the resulting solution was spectroscopically examined as before. This was repeated until the limits of the test were established. Table I. gives the lower limits of concentration at which the two principal lines of gallium could be thus detected.

TABLE I.—Spectroscopic Detection of Gallium.

	1.	2.	3.	4.
Grms. of gallium in 100 cc. . . .	0.0030	0.0046	0.0072	0.0154
Mg. of gallium in spark cup	0.0046	0.007	0.014	0.023
Gallium line, $\lambda = 4172$..	Faint.	Distinct.	Distinct.	Distinct.
Gallium line, $\lambda = 4033$..	Not visible.	Not visible.	Very faint.	Distinct.

These results show that, under the conditions described, 0.0046 mgrm. of gallium can be detected by ocular observation of the spark spectrum of a solution of gallium chloride, and that both of the principal lines of the spark spectrum are visible when 0.014 mgrm. of gallium as chloride is present.

Detection of Indium.—The procedure was the same as that for the detection of gallium. The lower limits of concentration at which the two principal lines of indium could be detected are given in Table II.

TABLE II.—Spectroscopic Detection of Indium.

	1.	2.	3.
Grms. of indium in 100 cc. . .	0.0009	0.0017	0.0043
Mg. of indium in spark cup . .	0.0013	0.0026	0.0065
Indium line $\lambda = 4511$..	Faintly visible.	Distinct.	Strong.
Indium line, $\lambda = 4102$..	Not visible.	Not visible.	Faintly visible.

These results show that it is possible, in this manner, to detect 0.0013 mgrm. of indium, and that both of the principal lines of the spark spectrum of indium are visible when 0.0065 mgrm. of indium as chloride is present.

Detection of Indium in the presence of Gallium.—It sometimes is the case that the lines of one element are masked or are rendered difficultly visible to the eye when a large amount of another element is present. For this reason the spark spectra of a series of solutions that contained both gallium chloride and indium chloride were

examined in order to determine the limit of visibility of the indium spectrum when a preponderating amount of gallium is present. The results are given in Table III.

TABLE III.—Spectroscopic Detection of Indium in the presence of Gallium.

	1.	2.	3.
Grms. in 100 cc.—			
Of gallium ..	3.12	2.91	2.89
Of indium ..	0.00191	0.0043	0.0074
Mg. in spark cup—			
Of gallium ..	3.1	2.9	2.8
Of indium ..	0.0019	0.0043	0.0073
Indium line—			
$\lambda = 4511$..	Faintly visible.	Distinct.	Distinct.
$\lambda = 4102$..	Not visible.	Faintly visible.	Distinct.
Per cent indium relative to gallium	0.06	0.15	0.26

From these results it is seen that the delicacy of the method of detecting indium by means of its spark spectrum is almost as great in the presence of a relatively large amount of gallium as it is when indium alone is present. When the gallium in the spark cup amounts to only 3 mgrms. the presence in it of 0.0019 mgrm. of indium, 0.06 per cent of the weight of the gallium may be detected by this method.

Detection of Gallium in the presence of Indium.—The spark spectra of solutions containing minute amounts of gallium chloride and relatively large quantities of indium chloride were next examined to ascertain the delicacy of the test for gallium (Table IV.).

TABLE IV.—Spectroscopic Detection of Gallium in the presence of Indium.

	1.	2.	3.	4.
Grms. in 100 cc.—				
Of indium	1.63	1.61	1.52	1.47
Of gallium	0.0030	0.0046	0.0134	0.0175
Mg. in spark cup—				
Of indium	1.63	1.61	1.52	1.47
Of gallium	0.0030	0.0046	0.0134	0.0175
Gallium line—				
$\lambda = 4172$..	Very faint.	Distinct.	Distinct.	Distinct.
$\lambda = 4033$..	Not visible.	Not visible.	Very faint.	Distinct.
Per cent gallium relative to indium ..	0.18	0.28	0.83	1.12

The delicacy of this method of detecting gallium is thus seen to be almost as great when a preponderating amount of indium is present as it is when gallium alone is examined. When the indium in the spark cup amounts to only 1.63 mgrms., the presence in it of 0.003 mgrm. of gallium, 0.18 per cent of the weight of the indium, may be detected by this method.

The Detection of Traces of Indium and Zinc by means of their Arc Spectra.

Although the spark spectrum was found to yield very satisfactory results in the detection of minute amounts of gallium and indium, it did not prove to be sufficiently sensitive for the detection of traces of zinc. For this reason the arc spectra of different mixtures of gallium, indium, and zinc were next studied, the spectra in this series of observations being photographed on non-halation orthochromatic plates manufactured by the Eastman Kodak Company. A pyrogallol developer prepared according to the formula of the same company gave excellent results.

Both a Steinheil grating spectrometer and a Hilger wave-length spectrometer were used in the beginning, but the Hilger instrument, being found to give much the stronger lines, was exclusively employed in the later measurements.

The arc was formed between graphite rods 12 mm. in diameter. The upper rod was roughly pointed at the end. A depression was hollowed out in the upper end of the lower terminal. Before these electrodes were used they were treated first with boiling hydrochloric acid and then with boiling water. A solution of the material to be examined was placed in the depression at the end of the lower rod and was then evaporated to dryness.

It was found that the faint lines due to minute amounts of zinc and indium showed most distinctly on the plates when the slit was fairly wide and the exposures were quite short, from five to ten seconds. Longer exposure strengthened the lines of the spectrum somewhat, but this was more than offset by the greater effect upon the plate of the continuous spectrum from the arc, which seriously reduced the contrasts in the photographs.

The indium line, $\lambda = 4102$, and the zinc line, $\lambda = 4811$, serve best to show the presence of these two elements because none of the strong lines due to the electrodes lies near them.

THE PURIFICATION OF GALLIUM.

Preliminary Examination of the Alloy of Gallium and Indium.

The alloy received from Mr. Stock was found to be rather slowly attacked by either nitric acid or hydrochloric acid alone. Hot aqua regia acted vigorously upon it, but complete solution resulted only after quite prolonged treatment.

One and three-tenth grms. of the alloy was placed in a solution of 7 grms. of potassium hydroxide in 50 cc. of water, and the liquid was heated to boiling. A rapid evolution of gas resulted, and this was accelerated when a piece of platinum was placed in contact with the alloy; yet even after the solution had been boiled for fifteen hours a considerable portion of the metal remained undissolved. This residue was next dropped into molten potassium hydroxide. The two substances reacted so violently that this method of treatment was abandoned because of the comparatively small amount of material at our disposal. It is possible, however, that this reaction might rapidly convert the gallium into a soluble compound of that element, and thus separate it from indium in a single simple operation.

To ascertain approximately the amount of indium in the alloy 6.6207 grms. of the material was dissolved in aqua regia, and the solution was boiled for several minutes with an excess of a solution of potassium hydroxide. The precipitate which resulted was collected on a filter, and yielded on ignition 0.6486 gm. of oxide which, had it been pure indium oxide, would have been equivalent to 0.5365 gm. of indium. This corresponds to 8.13 per cent of indium in the alloy. Spectroscopic examination showed, as was expected, that the precipitate was not pure indium, and, moreover, that it contained gallium. No further attempts were made at this stage of the investigation to determine the composition of the alloy because of the lack of analytical methods. The procedure for the quantitative separation of the constituents of the alloy that will be described later was developed only after all of the alloy had been dissolved and the gallium had been separated.

The Electrolysis of Solutions containing Gallium.

Boisbaudran obtained metallic gallium by electrolysis a solution of basic gallium sulphate in potassium hydroxide (*Ann. Chim. Phys.*, 1877, x., 100). Schucht makes the brief statement that "gallium, like zinc, is thrown completely at the negative pole in a pure state" (*Berg. und Hüttenmännische Zeit.*, 1880, xxxix., 121; *CHEMICAL NEWS*, 1880, xli., 280). Ehrlich electrolysed a "galliferous alkaline solution" from which metallic gallium was deposited in the form of fine needles (*Chem. Ztg.*, 1885, ix., 78; *CHEMICAL NEWS*, 1885, li., 115). Kunert electrolysed a solution of gallium hydroxide in potassium hydroxide (*Chem. Ztg.*, 1885, ix., 1826; *Ber.*,

1886, xix., 70); the current from ten large Bunsen cells deposited 0.1 gm. of pure gallium per hour.

Browning and Uhler electrolysed a solution of gallium hydroxide in sodium hydroxide, the metal separating as liquid globules at ordinary temperature, and in the form of a "tree" when the electrolyte was cooled to about 0° (*Am. Journ. Sci.*, 1916, xlii., 389).

Experimental examination of the deposition of gallium by electrolysis of a solution of gallium hydroxide in a solution of fixed alkali hydroxide showed that the metal is separated very slowly. Moreover, it seemed probable that gallium electrolytically deposited from a strongly alkaline solution would be contaminated with the alkali metal, a supposition that seems to be supported by the observation of Boisbaudran and Jungfleisch that gallium, thus prepared, decrepitates in hot water (*Comptes Rendus*, 1878, lxxxvi., 475), and by the statement of Browning and Uhler that the gallium "trees" liberate a gas when brought into contact with water. For these reasons it was sought to develop a method for the electrolytic deposition of metallic gallium from an acid solution, and to then study the separation of gallium from indium and zinc by this means.

The electrolytic deposition of indium from acid solution was satisfactorily developed a comparatively short time ago (Dennis and Geer, *Journ. Am. Chem. Soc.*, 1904, xxvi., 437; Thiel, *Ber.*, 1904, xxxvii., 175; Mather, *Journ. Am. Chem. Soc.*, 1907, xxix., 485). This element is the immediate group analogue of gallium. For this reason it seemed probable that the method that gave excellent results with indium, the electrolysis of an aqueous solution of the sulphate, might prove applicable to the deposition of gallium. If the electrolytic contained both gallium and indium it appeared to be reasonably certain that sharp separation of the two elements would not be effected by a single electrolysis, but it was hoped that fractional electrolysis would gradually first remove indium, and would finally yield deposits of gallium substantially free from indium.

A mixture of the hydroxides of gallium and indium was dissolved in sulphuric acid, 10 cc. sulph. acid (sp. gr. 1.14) added in excess, and the solution diluted to 350 cc. It was then electrolysed with a current of 4 ampères, the cathode of sheet platinum being 8×3 cm. At the end of three hours and forty minutes 0.0418 gm. of metal had been deposited on the cathode. This plate was then placed in another beaker containing dilute sulphuric acid, and was made the anode. The deposit readily dissolved as sulphate.

The spark spectrum of this solution showed gallium and indium lines of about equal intensity. A second deposit obtained from the first solution by electrolysis lasting three hours weighed 0.0108 gm. This was dissolved from the platinum cathode in the manner above described. The spark spectrum of its solution showed the gallium lines much more strongly than those of indium. The residual solution gave a strong spark spectrum of gallium but no indium lines.

The method was next used with a larger portion of material, 6.4113 grms. of the original alloy being employed. This was dissolved in dilute (1:10) sulphuric acid by immersing the alloy in 75 cc. of the acid, making contact with it by means of a platinum wire that projected slightly through the end of a glass tube, inserting in the acid the same platinum cathode as was used before, and electrolysed with the alloy as anode. The liquid alloy and the solution were stirred with a jet of air throughout the electrolysis. A potential difference of about 12 volts was maintained between the electrodes. This gave at the beginning a current of about 1 ampère, but when nearly all of the alloy had been converted to sulphate the current had dropped to about 0.1 ampère. A slight deposit which formed on the cathode during the solution of the alloy was found to consist of indium, gallium, and zinc.

The solution of the sulphates of these three metals, obtained in this manner by electrolysis, was evaporated to dryness, the residue was dissolved in water, and the solu-

tion was diluted to 100 cc. This was electrolysed, the anode being a sheet of platinum and the cathode a platinum rod that projected about 12 mm. into the solution. The solution was stirred by a jet of air. A current of 4 ampères yielded in two hours a deposit that weighed 0.0410 gm.

The spark spectrum of a solution of this deposit in hydrochloric acid showed strong lines of gallium and indium, but the lines of zinc were only faintly visible. The first solution was further electrolysed for two hours and ten minutes longer at 0.6 to 0.8 ampère, 0.0861 gm. being deposited on the cathode. The spark spectrum of the solution of this deposit in hydrochloric acid again showed strongly the lines of gallium and indium, and very faintly the lines of zinc. A further electrolysis of one hour and forty minutes at 0.6 ampère yielded 0.0545 gm. of deposit, which, when dissolved, showed strong lines of indium and gallium, whereas the zinc lines were scarcely visible.

A portion of the original solution from which these three deposits had been separated was concentrated, and its spark spectrum showed strong lines of gallium, faintly visible lines of indium, but no lines of zinc.

Ten further fractional electrolyses of this solution were then made, the time required for each deposit varying from 1.5 to 5 hours with a current of from 0.6 to 1.0 ampère. Each deposit was dissolved in hydrochloric acid, and the spark spectrum of the resulting solution was examined. In every case strong gallium lines were seen, but the spectrum of indium became gradually weaker, being scarcely visible in the last fractions.

Seven more fractions were deposited on a rotating rod of platinum which was bent into a wavy form for the purpose of stirring the solution. In the later fractions in this last series the gallium lines were strong and the a line of indium was faintly visible.

These results show that by means of fractional electrolysis of a slightly acid solution of the sulphates of gallium, indium, and zinc, zinc may be removed entirely, and gallium may be obtained almost free from indium.

Moreover, the electrolytic deposition of a small amount of metal from a slightly acid solution of the sulphates and the subsequent examination of the spark spectrum of the solution of this deposit in hydrochloric acid, affords a much more delicate qualitative test for traces of indium and zinc than can be obtained by direct examination of spark spectrum of the original solution.

For use in the further investigation of methods for the separation of gallium from accompanying elements about 25 grms. of gallium in the form of various salts was treated in such a way as to remove most of indium and zinc associated with it. This was done by boiling the solution with an excess of the solution of sodium hydroxide to remove indium as completely as possible. After the indium hydroxide had been removed by filtration the solution was made acid, and zinc was precipitated by the addition of a solution of potassium mercuric thiocyanate (see *prox.*). The precipitate of zinc mercuric thiocyanate was filtered off, and the mercury in the filtrate was precipitated as sulphide and was removed by filtration. The gallium in the filtrate was thrown down as the hydroxide by ammonium hydroxide. This gallium hydroxide was dissolved in sulphuric acid, and the solution was diluted to 800 cc. The solution then contained about 25 grms. of gallium as sulphate. The deposition of gallium by electrolysis from this solution under varying conditions showed certain interesting phenomena. When a portion of the solution was electrolysed with a cathode consisting of a rotating rod of platinum the liberated gallium formed a black suspension. Another portion of the solution was treated with sufficient sodium hydroxide to redissolve the gallium hydroxide, and this resulting solution was electrolysed with a cathode consisting of a sheet of platinum 8×3 cm., the current being from 2 to 4 ampères. During this electrolysis a portion of the metal formed a black suspension that settled very

slowly. The larger part of the metallic gallium was deposited on the cathode, and as the solution was kept above the melting-point of the metal globules of the gallium dropped from the cathode into a glass cup immediately beneath it. It was noticed that while the concentration of the gallium in this solution was still high a layer of reddish liquid collected at the bottom of the beaker at the end of nearly every period of the electrolysis. The electrolysis was carried on only during the day, and this reddish liquid collected to the depth of about 12 mm. during the night. The colourless liquid above this red layer was decanted through a filter and the red solution was then poured upon the filter. The red liquid could be seen flowing through the stem of the funnel, but when this struck the colourless liquid below, the red colour disappeared and a black suspension of metallic gallium formed in the liquid. When the concentration of gallium in the electrolyte became less the red liquid ceased to form. It seems probable that the red colour is due to a colloidal suspension of gallium which perhaps exists in this form only in a solution that contains a definite concentration of sodium hydroxide.

When the metal that was deposited by electrolysis was allowed to stand over night under water it became coated with a black film. If this metal is then placed in boiling dilute nitric acid for a time it regains its lustre, and retains it either under water or in the air. After the gallium had been treated for some minutes with boiling dilute nitric acid it was washed with water, was then caused to solidify by touching it with a particle of solid gallium, and this metal was kept over calcium chloride until used for the chlorination described below.

(To be continued).

THE COLOUR OF WATER.*

By WILDER D. BANCROFT, Ph.D.,
Professor of Physical Chemistry, Cornell University.

(Continued from p. 235).

IN still another paper Spring (*Bull. Acad. Roy. Belg.* [3], 1897, xxxi., 578) takes up the question of coloured compounds in the water, especially iron and humus. He determined the colour of pure water containing varying amounts of ferric oxide in solution or suspension. He did this by dissolving in aqua regia 0.700 gm. iron, which is equivalent to 1 gm. of Fe_2O_3 . After this had been evaporated to dryness on the water-bath, the product was dissolved in one litre of pure water distilled in a platinum apparatus. This yellow-brown solution was then diluted and examined after dilution in a tube five metres long. The data are given in Table V.

Fe_2O_3		Colour
1 : 10 000	..	Dark mahogany brown
1 : 100 000	..	Deep yellow
1 : 1 000 000	..	Yellow
1 : 2 000 000	..	Golden yellow
1 : 4 000 000	..	Yellow with trace of green
1 : 6 000 000	..	More yellow than green
1 : 8 000 000	..	Grass green
1 : 10 000 000	..	Green with trace of blue
1 : 12 000 000	..	Bluish-green
1 : 18 000 000	..	Greenish-blue
1 : 20 000 000	..	Blue with trace of green
1 : 24 000 000	..	Blue like pure water

* From this it follows that ferric oxide affects the blue colour so soon as its concentration gets above one part in

* From the *Journal of the Franklin Institute* clxxvii., No. 3

twenty-four millions. On the other hand, the Lake of Geneva contains one part of ferric oxide in about three million, but the water is blue and not yellow. The water of the Meuse is green and not yellow when it contains one part of ferric oxide in 1,500,000 of water. On the basis of analysis the Mediterranean should be brownish-yellow and not blue. From this it follows that the iron in these waters is not present in the same state as when a solution is made up in the laboratory. The point that has been overlooked is the effect of humic matter.

"In order to get suitable humic matter I have taken the black waters from the peat bog on the plateau of Baraque Michel, which is the highest plateau in Belgium. In this way I was certain of getting water uncontaminated by industrial products and containing only the brown-black compounds dissolved from the peat. It is therefore probable that the substances used corresponded closely and perhaps absolutely with the humic matter found in so-called pure, natural waters. In fact the water I used was as black as ink by reflected light but somewhat coffee-brown by transmitted light when observed in a twenty-centimetre layer. It can be filtered through filter paper, though very slowly, which proves that the brown substance is not entirely in solution. Its density was 0.99885 at 25.5°. Since pure water has a density at 0.99759 the peat water was 1.0012 times as dense. When examined with a spectroscope it gave a continuous, dark spectrum, in which one saw only red and green, but no blue and almost no yellow. It had a slight acid reaction. When evaporated in a platinum crucible, it left a black residue of 0.152 grm. per litre. After the carbonaceous matter had been destroyed by heating in the air the residue weighed 0.0238 grm. There was therefore 0.1282 grm. of organic combustible matter per litre of water. The small content of mineral matter (0.0238 grm./litre) indicated a water that has not flowed far through the earth. It is actually rain-water filtered slowly through a layer of peat.

"With this peat water the effect of humic matter on the colour of water has been determined. The data are given in Table VI., the concentrations being grms. of combustible matter per grm. of water.

"This table shows the extreme colouring power of humic matter. It has an effect about double that of ferric oxide if one compares equal weights. It is therefore easy to see the difficulties to be surmounted in a laboratory preparation of a really blue water, a pure water not containing more than one part in fifty million of organic matter.

"Filtered water from the Meuse contains about 1 grm. of combustible matter in nine thousand of water. If the combustible matter in the water of the Meuse were brown, soluble, humic material like that of the peat water, the river should look like a river of ink. The organic matter of the natural waters can no more be dissolved humic matter than the ferric compounds can be in a true state of solution. The concentration is more than a thousand times that which corresponds to the actual colour of the water.

TABLE VI.

Humic matter.	Colour.
1 : 500 000.. ..	Yellow-brown
1 : 1 000 000.. ..	Yellow
1 : 10 000 000.. ..	Yellowish green
1 : 20 000 000.. ..	Green
1 : 30 000 000.. ..	Bluish green
1 : 40 000 000.. ..	Greenish-blue
1 : 50 000 000.. ..	Blue

"From the preceding results one might expect to get a very dark brown liquid by mixing water containing a ferric salt with water containing humic material; but this is not the case. The water clears up and the rate of clearing is faster the more intense the light. . . . Under the influence of light the organic matter reduces the ferric salts to some extent, converting them into green

ferrous compounds, the colouring effect of which is not comparable with that of the ferric compounds. Owing to the absorbed oxygen the humic matter probably becomes more acid, and therefore forms salts more readily with the oxides of iron, alumina, &c., these [hypothetical] salts precipitating readily on account of their insolubility. The ferrous compounds remaining in solution are oxidised by the action of the air or by the oxygen dissolved in the water. When converted into ferric compounds they oxidise more of the unprecipitated organic matter. The ferric compounds therefore act in natural waters in the way hæmoglobin does in the blood of animals. . . . Hæmoglobin is looked upon as an oxygen carrier, taking it up from the lungs and distributing it through the system. The organic substances in the water are immersed in a medium which burns them while the body of an animal is irrigated by an oxidising liquid.

"The interaction of ferric salts and organic substances under the influence of light gives rise to an apparent equilibrium between the oxygen of the air and the ferrous compounds. If the intensity of the light increases, the proportion of ferric compounds decreases, because the organic substances will be oxidised more completely. Since the water will then contain smaller amounts of yellow or brown compounds, it will become more and more distinctly blue. On the other hand, if the intensity of the light decreases, the rate of the oxidation will decrease and the water will become more and more green, or even yellow, because the supply of colouring matter will not fall off with decreasing intensity of light. It is therefore easy to see why waters exposed to the sun are usually the bluest.

"If the amount of iron is very small relatively to that of the humic substances, these latter may be oxidised very slowly, in which case they will impart their brown, or even black, tint to the waters in which they are. The black waters of the equatorial regions of South America are said to contain 0.028 grm. of free humic acids per litre (Muntz and Marcano, *Comptes Rendus*, 1888, cvii., 231), a little more than one-fifth as much as the black peat water from the plateau of Baraque Michel in Belgium. In his paper on the colour of water, Wittstein (*Vierteljahresschrift Prakt. Pharmacie*, 1861, x., 346) has pointed out that the brown waters of Bavaria are remarkable for their softness. They contain almost no mineral matter.

"If the amount of iron is relatively large, there may be almost complete elimination of the organic matter. Almen (*Ber.*, 1871, iv., 750) has called attention to the purity of the great lakes of Sweden. Lake Wetteren is almost free from organic matter. Between these extremes there are the more common cases where the waters contain iron and organic substances in what one may call ordinary amounts. If one omits the instances where these waters are obviously turbid, their colour will be a dark green like those of most of our rivers, the Meuse, for instance, the waters of which are characterised by the absence of depth of colour and by a lack of that transparency which one finds in lakes or in the ocean. This is the effect that would be produced by the joint presence of iron and of organic substances.

"In so far as the waters of the river are exposed to the sunlight, a purification is continually taking place. If the river is sufficiently long the purification may even be complete before the waters reach the sea. This happens with the Nile. The upper waters are green in the 'dry season' and become more and more blue as one approaches the mouth of the river. In this case one can exclude the hypothesis of the change of colour being due to the influx of other waters. It is the water of the Nile itself which changes colour as it flows to the sea.

"In this way one can account for the deep blue colour of the high seas and in general of large masses of water, even when the analysis does not permit us to recognise any important differences. The ease with which humic matters combine with ferric oxide makes it clear why fer-

ruginous mineral deposits always contain organic matter. In fact, the limonites of the prairies and the ochres have been suggested as raw material for making bunic compounds."

The green often observed in swimming pools is undoubtedly due to suspended matter, though I can find no record of anybody having determined the exact nature of the suspended matter.

A special point has been discussed by Steuer (*Zoologische Jahrbücher, Abth. für Systematik, Geographie und Biologie der Thiere*, 1902, xv., 7). "The colour and the transparency of the water of the Danube bear so close a relation one to the other that we cannot treat them separately. We may draw the following general conclusions:—In winter the water is usually turbid and green to yellowish green; the melting snow and ice in the spring with the consequent rise of level, together with the influence of the drainage water, increase the turbidity and make the colour of the river even more yellow. That the colour of the Danube never is blue except in the song is well known. At best the water is greenish, and usually it is a dirty yellow. On the other hand, after a few windless days in late autumn, winter, and occasionally in spring, the water of the 'old Danube' become quite clear and appears a beautiful blue. Apart from the presence of plankton, the transparency and change of colour of the water vary with the suspended particles of sand or mud which are removed from the shore or the low islands by strong winds or high waves; are carried in by drainage water from the ground and also from the right bank; or are brought down by the melting snows in the spring."

The work of Aitken and Spring would seem to have settled the whole question were it not that Lord Rayleigh has recently brought the matter up again (*Nature*, 1910, lxxxiii., 48; *Scientific Papers*, 1912, v., 540). "A recent voyage around Africa recalled my attention to interesting problems connected with the colour of the sea. They are not always easy of solution in consequence of the circumstance that there are several possible sources of colour whose action would be much in the same direction. We must bear in mind that the absorption, or proper, colour of water cannot manifest itself unless the light traverse a sufficient thickness before reaching the eye. In the ocean the depth is of course adequate to develop the colour, but if the water is clear there is often nothing to send the light back to the observer. Under these circumstances the proper colour cannot be seen. The much admired dark blue of the deep sea has nothing to do with the colour of water, but is simply the blue of the sky seen by reflection. When the heavens are overcast the water looks grey and leaden; and even when the clouding is partial, the sea appears grey under the clouds, though elsewhere it may show colour. It is remarkable that a fact so easy of observation is unknown to many even of those who have written from a scientific point of view. One circumstance which may raise doubts is that the blue of the deep sea often looks purer and fuller than that of the sky. I think the explanation is that we are apt to make comparison with that part of the sky which lies near the horizon, whereas the best blue comes from near the zenith. In fact, when the water is smooth and the angle of observation such as to reflect the low sky, the apparent blue of the water is much deteriorated. Under these circumstances a rippling due to wind greatly enhances the colour by reflecting light from higher up. Seen from the deck of a steamer, those parts of the wave which slope towards the observer show the best colour for a like reason."

(To be continued).

A VALUABLE deposit of manganese has recently been discovered in Ecuador, near the town of San Antonio, in the province of Pichincha, South America. The deposit consists of a vein from 3 to 9 feet thick. The ore assays about 50 per cent manganese with silica and iron.

BOARD OF TRADE ANNOUNCEMENTS.

EXPORT OF COAL.

IN conformity with the policy of relaxing controls and facilitating the return to normal conditions, certain changes have recently been made in the conditions affecting the sale of coal for export, and it is now proposed, *inter alia*, to terminate the system of limited prices at present in operation in the case of coal shipped to France, Italy, and other Allied countries.

IMPORT RESTRICTIONS

The Board of Trade notify that general licences have been issued permitting the importation of the following articles:—Cocoa butter; oleo stearine; olive oil; fruit (fresh), except pears and grapes; articles of food containing sugar; aerated mineral and table waters (sweetened); gherkins in brine.

NOTES.

ROYAL INSTITUTION.—Next Tuesday, May 27, at 3 o'clock, Prof. W. H. Bragg will deliver the first of two lectures at the Royal Institution on "Listening Under Water" (the Tyndall Lecture). On Thursday, May 29, at 3 o'clock, Sir Valentine Chirol will give the first of two lectures on "The Balkans." The Friday Evening Discourse, on May 30, at 5.30 o'clock, will be delivered by Sir John Rose Bradford on "A 'Filter-passing' Virus in Certain Diseases." The closing Discourse of the Session will be given on June 6 by Prof. Sir Ernest Rutherford on "Atomic Projectiles and their Collisions with Light Atoms." On Saturday, May 31, at 3 o'clock, Mr. J. M. Price will give the first of two lectures on "The Italian Front," illustrated by cinematograph films lent by the Italian Government.

EYE PROTECTION IN WELDING OPERATIONS.—The ideal goggle for use in welding is that which permits of greatest visibility, and at the same time excludes heat rays and ultra-violet rays. The author shows the spectra of a number of commercially available glasses and combinations of glasses, and explains how such spectra may be used to discriminate between various filters. The selection of coloured glasses to yield clearest definition with sufficient obscuration of glare is necessary where there are powerful visible rays. This selection is a matter for experts. In addition heat-absorbing glass may be necessary. Clear glass (but not quartz or natural rock crystal) is a protection against ultra-violet rays which are not too intense. Dark amber or dark amber green glasses are an absolute filter for ultra-violet rays; glasses showing blue or violet tints should be avoided unless they are needed to obscure other colours.—(W. S. Andrews, *General Electric Review*, Dec., 1918).—*Technical Supplement*.

At the recent meeting of the Faraday Society and the Röntgen Society, Sir Robert Hadfield and Mr. S. A. Main gave an account of the results of the X-ray examination of the carbon electrodes used in steel making furnaces. These electrodes vary in size and reach no less than 20 inches in diameter; if during a melt portions fall into the steel-bath the whole cast may become spoilt or wasted. Sections were cut about 1 inch in diameter and submitted to X-ray examination, and the results, which were of course of a preliminary nature, do not appear to have been very encouraging. Where a uniform structure was noticed in the radiograph the "service quality" of the electrode is reported as "fairly good," while another electrode that gave by X-ray examination a coarse structure very full of opaque grains gave in service an excellent result. Faults in manufacture such as cracks and flaws are, of course, revealed. Further work on the subject will probably yield valuable results.

A NOVEL form of CO_2 indicator has recently been evolved that presents several new features, the chief being its extreme simplicity; there is no complicated mechanism to get out of order, and the percentage of CO_2 is read by the height of a column of water. The instrument can be fixed in the stokehold so that the fireman can see at a glance what is taking place in the furnace. The indications are said to be accurate to within 1 per cent. A list of representative purchasers shows that it is being used by most of the prominent firms in the country. Full particulars can be obtained from W.R. Patents, Ltd., 8, Old Jewry, London, E.C.

THE International Institute of Agriculture publishes a note on the "Extent of Land under Winter Crops of Cereals and Oil-seeds in the Northern Hemisphere," and it is stated that the area under wheat in the United States has been increased by 16 per cent as compared with that of last year, while, for every country except this, there appears a decided decrease in the wheat areas even amounting to a very large decline in the case of British India. As regards the crop condition on April 1 it is reported as a good one for wheat in the United States and for oats in Ireland. It is classed as satisfactory for wheat in England and Wales. In Italy, as well as for crops in general, the condition was an average one at the date named, while in Scotland the wheat was reported as below the average in condition.

THE demand for "power" for the manufacture of munitions, combined with the world shortage of coal, has made it necessary to systematically survey the available water power in various parts of Europe. The second report of the Water-power Committee of the Conjoint Board of Scientific Societies has just been published. Surveys of the water-power available in India, Africa, and the Colonies are being made, and all the information collected. The probable outcome of this work will be the employment of a deal of power to useful purposes instead of allowing it to be wasted. Much has been done in this direction in Germany and Austria during the war. Water-power in France is being applied largely to the electrification of railways. In Great Britain and Ireland the present total developed power is 210,000 B.H.P. The discovery of large deposits of bauxite in British Guiana and the fact that much water-power is available in the locality gives good prospect of this colony becoming an important producer of aluminium. It is recorded that one river alone offers the possibility of two and a half million B.H.P. In Rhodesia the estimated power at Victoria Falls at low water is 350,000 B.H.P.; at flood power this would be greatly exceeded. The report concludes by pointing out the necessity for training engineers to undertake the work, and the Committee recommends that the matter be brought to the notice of the Minister of Education and the Secretary for Scotland.

NOTES FROM FOREIGN SOURCES

Spectrographic Study of the Ash of Marine Plants.—Eugène Cornec.—It is known that a very large number of elements are to be found in traces in sea water, and it seems probable that the selective power of marine plants is not limited to iodine, so that the ash of them should contain many elements. The author has subjected the ash of such plants, after extraction with water and hydrochloric acid, and also the precipitates corresponding to the different analytical groups, to spectrographic examination, the complete study of the spectrograms being limited to the ultraviolet region comprised between 2500 and 3500 Å.U. Without being absolutely general the method is applicable for most of the heavy metals, and specially for the rare metals. He has thus detected the presence of metals, which he has classed together in three groups.

In the first group he includes those which are already known to exist in marine plants, such as silver, arsenic, cobalt, copper, &c. The second group contains those which have been detected in sea water—bismuth, tin, gallium, molybdenum, gold; while the third group consists of such elements as have not been found either in sea water or in marine plants. These are antimony, germanium, beryllium, titanium, tungsten, and vanadium. There are no indications of the presence of elements of the platinum group, nor of those of the rare earths. The absence of thallium and indium is specially noteworthy. Gold, bismuth, gallium, and germanium exist only in spectrographic traces.—*Comptes Rendus*, 1919, cxlviii., 513.

Evolution of Gas when Fused Sodium Hydroxide is Dissolved in Water.—W. H. Schramm.—It has frequently been observed that when fused sodium hydroxide is dissolved in water a gas of piercing odour is evolved. The author has shown that this effect is produced by the action of a very small quantity of oxygen which is set free by the decomposition of a chemical compound and escapes mixed with air. The compound in question is an alkali compound of a higher oxidation product of iron, possibly sodium perferite, $\text{Fe}_2\text{O} \cdot \text{Na}_2\text{O}$.—*Chemiker Zeitung*, 1919, xliii., 69.

Determination of Sulphuric Acid and Sulphates.—M. G. Meillère.—Two chief causes of error in the quantitative determination of SO_4 as BaSO_4 are due to the energy with which the precipitate and the filter-paper both retain the excess of barium salt used as precipitant by a phenomenon of adsorption. The separation and washing of the precipitate by centrifugation, weighing the sulphate in the tube itself, does away with one of these errors but not the other. The washings can be much hastened by working in a solution acidified with a little acetic acid at a temperature as near 100° as possible. A double filter must be used and gentle suction must be employed. To avoid the use of too much barium salt in the case of the determination of H_2SO_4 , baryta water may be used and a trace of phenolphthalein may be added; the coloration should persist some minutes after the addition of baryta water. Then the liquid must be acidified with acetic acid, kept on the water-bath for an hour or two, and then filtered.

Existence of Isotungstic Acid.—P. Barbe.—In 1847 Lanreut described an isotungstic acid, which Gerber also obtained and investigated in 1917. When metatungstic acid was boiled with excess of ammonia, or when an ammoniacal solution of certain purified tungstic acids was evaporated, ammonium isotungstate was said to be formed. When calcined it gave a dark green or even black tungstic anhydride of composition $6\text{WO}_3 \cdot 2(\text{NH}_4)_2\text{O} \cdot 7\text{H}_2\text{O}$, which gave for the value of $\frac{\text{W}}{(\text{NH}_4)_2\text{O}}$ 3.0, whereas the value for a paratungstate would be 2.3 to 2.4. Isotungstic acid, when reduced by hydrogen, gave a crystalline metallic product, and the atomic weight of the metal appeared to be 187, or three units more than the officially recognised number. Gerber concluded that isotungstic acid contains, besides tungsten, a new substance of higher atomic weight, which he called neotungsten, but this result was not confirmed by spectroscopy. The author has repeated the experiments, preparing the isotungstate by three different methods and determining the ratio of WO_3 to $(\text{NH}_4)_2\text{O}$ in each case. He finds that the presence of sodium raises the value of the ratio from 2.4 to 3.0, and at the same time accounts for the other characteristic properties of isotungstic anhydride, including the dark green colour. Thus the substance which Gerber called ammonium isotungstate is really a double tungstate of ammonia and soda, and the author believes that there is no real reason for suggesting the existence of another tungsten of higher atomic weight than that officially recognised.—*Moniteur Scientifique*, 1919, 73.

CORRESPONDENCE.

ANALYTICAL EXAMINATION OF ACORNS
AND HORSE CHESNUTS.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS, cxvii., 244 (Nov. 16, 1917), there occurs an abstract of a paper on this subject by J. L. Baker and H. F. E. Hulton, in which it is stated that no diastase occurs in the acorn either before or after germination. On p. 177 of "The Principles and Practice of Brewing" (W. J. Sykes, 1897) it is stated:—"Hops, like all other plants, contain diastase, but this point appears to have been overlooked until attention was called to the fact by Brown and Morris (*Journ. Federated Inst. Brewing*, 1897, p. 233). The enzyme could only be extracted by water after removal of the tannin contained in the hops. A similar phenomenon was observed by Baranetzky with reference to acorns" (Sachsse, "Agricultural Chemistry," p. 364).

If a plant does not contain diastase, what enzyme does it contain which converts starch into soluble carbohydrates?—I am, &c.,

CHARLES E. FRANCK, A.I.C.

39, Albert Street, Shrewsbury.

MEETINGS FOR THE WEEK

Monday, May 26.

Royal Geographical Society, 8.30. "Recent Journeys in Manchuria," by Capt. A. de C. Sowerby.

Royal Society of Arts, 4.30. "A New Prime Mover of High Efficiency and British Origin," by Capt. Frank E. D. Acland.

Tuesday, May 27.

Royal Institution, 3. "Listening under Water," by Prof. W. H. Bragg.

Institution of Gas Engineers, 10.30 a.m.

Royal Horticultural Society, 3. "Some Irish Gardens," by J. G. Weston.

Institution of Electrical Engineers, 6.30. (At Caxton Hall, Westminster). Discussion—Electrical and Engineering Equipment of Modern Small Houses.

Royal Photographic Society, 7. "Spiders—Their Structure and Habits," by Dr. G. H. Rodman.

Royal Society of Arts, 4.30. "Science and Industry in Australia," by Lieut.-Colonel the Hon. Sir John McCall.

Wednesday, May 28.

Institution of Gas Engineers, 10.30 a.m.

Royal Society of Arts, 4.30. "Glass-making before and during the War," by H. J. Powell.

Royal Society of Medicine, 8.30. "How to Start and Succeed in General Practice," by Dr. Steele-Perkins.

Thursday, May 29.

Royal Society, 4.30. (Croonian Lecture). "Biological Significance of Anaphylaxis," by Dr. H. H. Dale.

Royal Institution, 3. "The Balkans," by Sir Valentine Chirol.

Institution of Gas Engineers, 10.30 a.m.

Institution of Electrical Engineers, 2.30. (Annual Meeting at Royal Society of Arts).

Friday, May 30.

Royal Institution, 5.30. "A 'Filter-passing' Virus in certain Diseases," by Sir John Rose Bradford.

Institution of Mechanical Engineers, 6.

Institute of Chemistry, 4.30. (Council Meeting).

Saturday, May 31.

Royal Institution, 3. "The Italian Front," by J. M. Price.

Analytical Chemist wanted. Must be fully trained and have good general Analytical experience. Applications must contain full particulars of age, training, experience, and salary required, and must be made in writing to General Works Manager, Messrs. Lever Brothers Limited, Port Sunlight, Cheshire.

Chemist, demobilised, three years' Technical College training and one year works experience, in order to regain experience, lost Army service, would communicate with Analyst of extensive practice with view to Post as Pupil Assistant for limited period.—Address, R. B., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Chemist desires Employment in London. During War, Chief Chemist in a Canadian T.N.T. plant. Two years Organic Research Work. Would be content to start as Assistant in any branch of Chemistry.—Address, S. L., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Chemist, with four years' training at Finsbury Technical College, having taken active service immediately upon completion of course, is now demobilised and seeks Engagement.—Address, A. F. G., 21, Chestnut Road, West Norwood, S.E.

Junior Assistant Chemist wanted for the Fuel Research Laboratory. One preferred with B.Sc. Degree, but not absolutely essential. Should have good knowledge of Geology and Palaeobotany. State particulars of training and experience, age, and salary required.—Address, F. R., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

RESEARCH.—Repatriated prisoner, honours graduate, Physical, especially Electro-chemistry and Physics, 17 years in practice, record of successful inventions, experience in organising and running manufacture in England and Germany, before war practising consultant, seeks suitable position.—Address, R. R., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Student, finishing four year Associate Course in Applied Chemistry in June next, desires to communicate with firms re suitable appointment. Foreign or Colonial post desirable.—Address, "Student," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

University man (Demobilised Officer), first class in Chemistry and Mathematics at London Inter-B.Sc., and excellent testimonial from his Professor, desires situation, either of Secretarial nature or in some capacity utilising above qualifications.—Address, U. M., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

RESEARCH FELLOWSHIP.

SCOTTISH TANNERS' FEDERATION.—Applications are invited for Post as RESEARCH FELLOW to the Scottish Leather Trade. Salary £400 per annum with a financial interest, to be mutually agreed upon, in discoveries of commercial value.—Address, S. T. F., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

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THE CHEMICAL NEWS

VOL. CXVIII., No. 3085.

A METHOD FOR THE VOLUMETRIC ESTIMATION OF SULPHATES.

By A. C. D. RIVETT, M.A., D.Sc.

It is possible to estimate sulphates volumetrically by a simple method which, though of limited applicability, is very useful as a works test in suitable solutions. The method depends upon the fact that moist precipitated barium oxalate reacts quantitatively by double decomposition with dissolved sulphates of certain metals to give barium sulphate and the soluble oxalates of these metals. The latter may be titrated in the filtrate with potassium permanganate.

The reaction with barium oxalate is not rapidly completed at ordinary temperature, but provided the amount of sulphate present be not too great, a few minutes boiling will suffice to complete it. This is apparent from the first set of figures (Table I.). To obtain these a known weight (0.476 grm.) of anhydrous sodium sulphate was dissolved in 100 cc. of water, and treated with excess of precipitated barium oxalate under the conditions quoted in the second column. If the mixture had been heated it was then cooled under the tap and made up to 200 cc. exactly. A portion of the solution was run through a filter, and a known volume pipetted off and titrated with decinormal permanganate in the usual manner. An accuracy to 1 part in 200 may be considered satisfactory in view of possible errors in procedure and the fact that the salts used were not of the highest purity.

TABLE I.

No.	Conditions.	Wt. of Na_2SO_4 found.
1.	Mixture shaken intermittently in the cold for five minutes ..	0.452
2.	Shaken continuously in the cold for five minutes	0.459
3.	Brought to boiling-point	0.469
4.	Boiled for five minutes	0.475
5.	Boiled for ten minutes	0.473
6.	Boiled for fifteen minutes	0.474

It appears that five minutes boiling is sufficient to complete the reaction in solutions containing sodium sulphate in amount approximating to half a grm. in 100 cc.

Since precipitated barium oxalate has quite an appreciable solubility in pure water, it is clear that in very dilute solutions of sulphate error will be introduced on this account. This will, however, be the case over only a limited range, for with increase in concentration of sulphate there will be corresponding increase in concentration of sodium (or other) oxalate formed, and the ionic concentration of the negative radicle will be sufficiently great to repress the solubility of barium oxalate below the limit of experimental error. In obtaining the figures given in Table II. the detailed procedure has in every determination been the following:—

An amount of sodium sulphate (gravimetrically standardised against barium sulphate) was weighed and dissolved in 150 cc. of water; precipitated barium oxalate was added as a moist paste in amount equal to about three times that calculated to be necessary; the mixture was boiled for five minutes, cooled under the tap, and made up to exactly 250 cc.; a portion was run through a filter, and a definite volume titrated with decinormal permanganate. An approximate correction, readily determined with sufficient accuracy, was made for the volume occupied in the 250 cc. flask by the solid precipitates. This procedure avoids delay in washing the precipitate.

TABLE II.

No.	Wt. Na_2SO_4 taken.	Wt. Na_2SO_4 found.	Percentage error.
7.	None	0.021	—
8.	0.0735	0.0818	+1.3
9.	0.214	0.221	+3.3
10.	0.327	0.336	+2.8
11.	0.563	0.569	+1.1
12.	0.760	0.764	+0.5

Taking 1 in 200 as satisfactory accuracy it appears that the solubility of barium oxalate may be neglected only when the solubility with which it is boiled contains more than 0.75 grm. of sodium sulphate in 150 cc.

With amounts above this the results are quite satisfactory, as will be seen from the next series of analyses in Table III.

TABLE III.

No.	Wt. Na_2SO_4 taken.	Wt. Na_2SO_4 found.	Percentage error.
13.	0.917	0.921	+0.4
14.	1.262	1.263	+0.1
15.	1.326	1.325	-0.1
16.	1.335	1.330	-0.4
17.	1.463	1.497	+0.1
18.	1.719	1.723	+0.2
19.	2.047	2.036	-0.5

If the amount of sodium sulphate exceeds about 2 grms. in the 150 cc. boiled with barium oxalate, the method is just as accurate provided that the time of boiling be increased in order to complete the reaction. This is shown in the three results given in Table IV.

TABLE IV.

No.	Wt. Na_2SO_4 taken.	Time of boiling.	Wt. Na_2SO_4 found.	Percentage error.
20.	3.079	5 minutes.	3.034	-1.5
21.	5.013	5 minutes.	4.889	-2.5
22.	4.964	25 minutes.	4.949	-0.3

It is therefore advisable in order to save time in a routine works test of a liquor to take an amount containing from 1 to 2 grms. calculated as sodium sulphate, and to boil this with barium oxalate in a volume of 150 cc.

If other salts be present along with sulphates, double decomposition may take place to some extent between them and the barium oxalate, and so lead to high results. This is confirmed by the analyses given in Table V.

TABLE V.

No.	Wt. Na_2SO_4 taken.	Other salt present.	Wt. Na_2SO_4 found.	Percentage error.
23.	1.326	None	1.325	-0.1
24.	1.326	2 grms. KNO_3 ..	1.324	-0.15
25.	1.326	10 grms. KNO_3 ..	1.345	+1.4
26.	1.326	25 grms. KNO_3 ..	1.400	+5.6
27.	1.326	15 grms. NH_4NO_3	1.396	+5.3
28.	1.326	{ 20 grms. hydrated $\text{Na}(\text{C}_2\text{H}_3\text{O}_2)$.. }	1.343	+1.3

In such cases, where the amounts of other salts remain fairly constant (as they would in a works liquor) and are not excessively greater than the sulphate, an empirical constant correction may be introduced with sufficient accuracy.

This volumetric method of estimating sulphates in solution was used with success last year, practically as described and with an empirical correction, in one of H.M.'s factories where it was necessary to determine the sulphate content of liquors containing principally sulphates and nitrates of sodium and ammonium. It is very much more rapid than the gravimetric estimation as barium sulphate, and the analyses given in Table VI. carried out by one of the laboratory testers show the sort of agreement obtained between the two methods.

TABLE VI.

Volumetric.	Gravimetric
6.04	6.11
6.11	6.12
6.35	6.37
5.93	5.99
6.36	6.32
6.08	6.05

The limitations of the method are obvious. It is inapplicable in acid solutions, and cannot be used to determine sulphates of metals forming insoluble oxalates or sulphates in presence of salts containing radicles capable of forming insoluble barium salts. The presence of halides is objectionable in preventing accurate titrations with permanganate. There will, however, be many works to which the method may be applied with accuracy and considerable saving of time.

Chemistry Department, University of Melbourne,
March 31, 1919.

DETERMINATION OF PHOSPHORUS IN PHOSPHOR TIN.

By WILLIAM LORD.

THE following adaption of Oettel's method for determining phosphorus in phosphor bronze has been applied to samples of commercial phosphor tin containing up to 6 per cent phosphorus and found very accurate and rapid.

A method in which the metal was dissolved in aqua regia, the tin precipitated as sulphide, and the phosphorus determined as $Mg_2P_2O_7$ in the filtrate, was found to be worthless, the bulk of the phosphorus being carried down with the tin sulphide. In one sample containing 2.6 per cent P no trace of the element could be found in the filtrate from the tin sulphide, but on examination of the precipitate the whole of the phosphorus was found.

An attempt was made to determine the phosphorus by oxidising with nitric acid and igniting the $SnO_2 + P_2O_5$ with KCN, after filtering through double filter-papers, as in the ordinary determination by Oettel's method, but extremely low results were obtained, through the reducing action of the filter-paper on the P_2O_5 during ignition and the consequent loss of phosphorus.

1 gm. of the finely divided metal is treated in a large porcelain crucible with concentrated HNO_3 , and heated on a water-bath until oxidation is complete. This is indicated when nitrous fumes cease to be evolved and a perfectly white residue remains in the crucible, in which no hard metallic particles can be felt with a glass rod.

Oxidation is often very slow if the metal is not in a state of fine division, the larger particles quickly becoming coated with a protective layer of metastannic acid.

The mass is taken to complete dryness and mixed with six times its weight of pure KCN. The crucible is covered and gradually heated to dull redness for fifteen minutes, by which time reduction of tin oxide to metallic tin will be accomplished, together with a quantitative conversion of the phosphoric anhydride to potassium phosphate. Towards the end of the fusion it is quite easy to collect the tin into one globule by imparting a rotary motion to the crucible, and this greatly facilitates the subsequent filtration. When cold the melt is extracted with steam, the crucible being placed upright in a tall beaker, and a jet of steam blown into it from a boiler. A clean paint can fitted with a cork and delivery tube serves well for the purpose. By this means the fusion may be completely extracted in five or six minutes with very little trouble. The button of tin is filtered off, and the filtrate acidulated with HCl, to decompose KCN and $KCNO$. Considerable HCN is evolved, and this is best performed under a good hood. After boiling to expel HCN a rapid stream of H_2S is led through the hot solution to remove any tin which may have escaped separation previously,

and the precipitate filtered off. A little bromine water is added to the filtrate, which is then evaporated to a bulk of 50 cc. and cooled. It is made slightly ammoniacal, and if any precipitate of iron or aluminium hydroxides occurs this should be filtered off, dissolved in HCl, and reprecipitated, the filtrate being added to the main solution. 10 cc. of magnesia mixture are added, and the solution stirred until the formation of crystalline magnesium ammonium phosphate commences, when stirring should be stopped, and 10 cc. of strong ammonia added. It is best to allow complete precipitation by standing overnight in water.

The precipitate is collected on asbestos, in a Gooch crucible, and washed with 2 per cent ammonia containing ammonium nitrate.

After drying in an air-bath, the crucible is heated at gradually increasing temperature, and finally ignited at the back of the muffle, until a perfectly white mass of $Mg_2P_2O_7$ is obtained. This is seldom accomplished if the precipitate is ignited damp. The percentage of phosphorus is computed in the ordinary way from the weight of $Mg_2P_2O_7$ obtained.

The following mixture (Price and Mead, "Technical Brass Analysis") was used for precipitating the phosphorus:—

Ammonium chloride		11 parts
Magnesium chloride		28 parts
Water		130 parts
Ammonia (1 : 1)		70 parts

1 cc. = 0.01 gm. P.

THE COLOUR OF WATER.*

By WILDER D. BANCROFT, Ph.D.,
Professor of Physical Chemistry, Cornell University.
(Concluded from p. 250).

"THE real colour of ocean water may often be seen when there are breakers. Light, perhaps directly from the sun, may then traverse the crest of the waves and afterwards reach the observer. In my experience such light shows decidedly green. Again, over the screw of the ship a good deal of air is entangled and carried down, thus providing the necessary reflection from under the surface. Here also the colour is green.

"The only places where I have seen the sea look blue in a manner not explicable by reflection of the sky were Aden and Suez. Although the sky was not absolutely overcast, it seemed that part at any rate of the copious, if not very deep, blue was to be attributed to the water. This requires not only that the proper colour of the water should here be blue, but also the presence of suspended matter capable of returning the light, unless indeed the sea bottom itself could serve the purpose.

"The famous grotto at Capri gives an unusually good opportunity of seeing the true colour of the water. Doubtless a great part of the effect is due to the eye being shielded from external glare and so better capable of appreciating the comparatively feeble light which has traversed considerable thicknesses of water. The question was successfully discussed many years ago by Melloni, who remarks that the beauty of the colour varies a good deal with the weather. The light which can penetrate comes from the sky and not directly from the sun. When the day is clear the blueness of the sky co-operates with the blueness of the water.

"That light reflected from the surface of a liquid does not exhibit the absorption colour is exemplified by brown peaty water such as is often met with in Scotland. The sky seen by reflection is as blue as if the water were pure. But an attempt to illustrate this fact by experiment upon quite a small scale was not at first successful. A large white photographic dish containing dark brown oxidised

* From the *Journal of the Franklin Institute* clxxxvii., No. 3

'pyro' was exposed upon the lawn during a fine day. Although the reflected light certainly came from the clear sky, the colour did not appear pronounced, partly in consequence of the glare of the sunshine from the edges of the dish. The substitution of a dish of glass effected an improvement. But it was when the eye was protected from extraneous light by the hands, or more perfectly by the interposition of a pasteboard tube held close up, that the blue of the reflected light manifested its proper purity. It would seem that the explanation is to be sought in diffusion of light within the lens of the eye, in consequence of which, especially in elderly persons, the whole field is liable to be suffused with any strong light finding access.

"As regards the proper colour of pure water, an early opinion is that of Davy, who, in his *Salmonia*, pronounces in favour of blue, basing his conclusion upon observations of snow and glacier streams. The latter, indeed, are often turbid, but deposit the ground-up rock which they contain when opportunity offers, as in the Lake of Geneva. A like conclusion was later put forward by Bunsen on the basis of laboratory observations. The most elaborate experiments are those of Spring, who, in a series of papers published during many years, discusses the difficult questions involved. He tried columns of great length—up to 26 metres; but even when the distance traversed was only 4 or 5 metres he finds the colour a fine blue only to be compared with the purest sky-blue as seen from a great elevation. But when the tubes contain ordinary water, even ordinary distilled water, the colour is green, or yellow-green, and not blue.

"The conversion of the original blue into green is, of course, explicable if there be the slightest contamination with colouring matter of a yellow character—i.e., strongly absorbent of blue light. Spring shows that this is the effect of minute traces—down to one ten-millionth part—of iron in the ferric state, or of humus. The greenness of many natural waters is thus easily understood. Another question examined by Spring is not without bearing upon our present subject—viz., the presence of suspended matter. I am the better able to appreciate the work of Spring, that many years ago I tried a variety of methods, including distillation *in vacuo*, in order to obtain water in the condition which Tyndall described as 'optically empty,' but I met with no success. Spring has shown that the desired result may be obtained by the formation within the body of the liquid of a gelatinous precipitate of alumina or oxide of iron, by which the fine particles of suspended matter are ultimately carried down.

"Perhaps the most telling observations upon the colour of water are those of Count Aufsess, who measured the actual transmission of light belonging to various parts of the spectrum. The principal absorption is in the red and yellow. In the case of the purest water there was practically no absorption above the line F, and a high degree of transparency in this region was attained even by some natural waters. That these waters should show blue, when in sufficient thickness, is a necessary consequence.

"In my own experiments, made before I was acquainted with the work of Aufsess, the light traversed two glass tubes of an aggregate length of about 4 metres (12 feet). On occasion the light was reflected back so as to traverse this length twice over. I must confess that I have never seen a blue answering to Spring's description when the original light was white. For final test I was careful to employ the light of a completely overcast day, which was reflected into the tubes by a small mirror. The colour, after transmission, showed itself very sensitive to the character of the original source. The palest clear sky of English winter's day gave a greatly enhanced blue, while, on the other hand, isolated clouds are usually yellowish, and influence the result in the opposite direction. I should myself describe the best colour of the transmitted light on standard days as a greenish blue, but there is some variation in the use of words, and perhaps

in vision. Some of my friends, but not the majority spoke of blue simply, but all were agreed that the blueness of a good sky was not approached. The waters tried have been very various. Sea-water from outside the grotto of Capri, from Suez, and from near the Seven Stones Lightship off the Cornish Coast, I owe to the kindness of friends. Of these the two former showed a greenish-blue, the latter a full, or perhaps rather yellowish, green, and these colours were not appreciably modified after the water had stood in the tubes for weeks. It is important to remember that the hue may to some extent depend upon the thickness. It is quite probable that in a greatly increased thickness the Capri and Suez waters would assume a more decided blue colour. But I do not think the Seven Stones water could so behave, the colour, with 12 feet, seeming to involve the absorption of blue light. Further observations on greater depths of sea-water would be desirable. A naval son informs me that off the coast of Greece a plate lying in six fathoms of water looked decidedly blue, although the sky was a dirty grey. I have doubts whether this would be generally the case in the Mediterranean; the green due to moderate thicknesses seems too decided.

"Of natural fresh waters that I have tried, none were better than that from a spring in my own garden. This water is hard, but bright and clear, and it shows a greenish-blue, barely distinguishable from that of the Capri and Suez water. Distillation does not improve the blue. Neither did other treatments do any good, such, for example, as partial precipitation of the lime with alkali, or passage of ozone with the idea of oxidising humus. Wishing to try water of high chemical purity, I obtained—through the kind offices of Sir J. Dewar—water twice distilled from alkaline permanganate, and condensed in contact with silver, but the colour was no bluer. In the light of this evidence I can hardly avoid the conclusion that the blueness of water in length of 4 metres has been exaggerated, especially by Spring, although I have no reason to doubt that a fully developed blue may be obtained at much greater thicknesses. I should suppose that sufficient care has not been taken to start with white light. It may be recalled that overcast days are not so common in some parts of the world as in England.

"A third possible cause of apparent blueness of the sea must also be mentioned. If a liquid is not absolutely clear, but contains in suspension very minute particles, it will disperse light of a blue character. Although, undoubtedly, this cause must operate to some extent, I have seen no reason to think that it is important. But the existence of three possible causes of blueness complicates the interpretation of the phenomena. Hitherto, observers have not been sufficiently upon their guard to distinguish blueness having its origin in the sky from blueness fairly attributable to the water itself."

The question at issue seems to be whether Lord Rayleigh's negative results are to outweigh Spring's positive results. On general principles, there are so many ways of failing in an experiment that a positive result usually outweighs any number of negative ones. On the other hand, Lord Rayleigh is such a careful worker that his conclusions are not to be rejected hastily. The fact that he does not give details to the same extent that Spring does cannot be charged against him because he was delivering an address before the Royal Institution, while Spring was writing a series of scientific papers. The whole question must therefore be considered as open for the present, though one may at least hope that Spring will prove to be right.

Beebe seems to feel that the colour of water is entirely an optical illusion ("Sea-Wrack," *Atlantic Monthly*, 1918, 481). "One finds numerous examples of these sensory deceptions at sea. The wind flutters the fins of the flying fish and we think they actually fly. The tropic sea, under the palest of green skies, is saturated ultramarine, save where the propellers churn it to pea-green, yet in our bath the water is clear and colourless. . . . The great unlovely bow rose and reached forward and settled, until

as I lay face-downward our speed seemed increased many-fold. And I wondered if the wooden expression which always marked the figure-head ladies and gods had not its origin in the hypnotic joy of forever watching the molten cobalt crash into alabaster, this into emerald, then to merge again into the blue, which is a hue born of depth and space and not of pigment."

GALLIUM.*

By L. M. DENNIS and J. ALLINGTON BRIDGMAN.

(Continued from p. 248).

The Distillation of Gallium Chloride.

Zinc chloride boils at 730° . Indium trichloride volatilises very slightly at 440° and only slowly at 600° . Gallium trichloride melts at 75.5° and boils at $215-220^{\circ}$. These

with a view to ascertaining whether gallium chloride free from zinc and indium might be thus prepared.

A preliminary chlorination and distillation was made with a portion of the original alloy. A glass tube of about 2 cm. diameter was slightly bent in the middle, and a portion of the alloy (3.3962 grms.) was placed in the lowest part of the bent tube. A small oven constructed of asbestos board was placed around this portion of the tube (Dennis, "Gas Analysis," p. 202). Dry chlorine was passed through the tube, and the oven was heated to 240° . Some of the resulting chlorides distilled and condensed in the cold portion of the tube beyond the oven. The spark spectrum of this material showed faint lines of indium and zinc and strong lines of gallium.

An apparatus of the form shown in Fig. 1 was then constructed, the tube A being of Jena glass. About 4 grms. of the alloy was placed in A, dry chlorine was passed into the tube, and the lower end of A was heated to start the

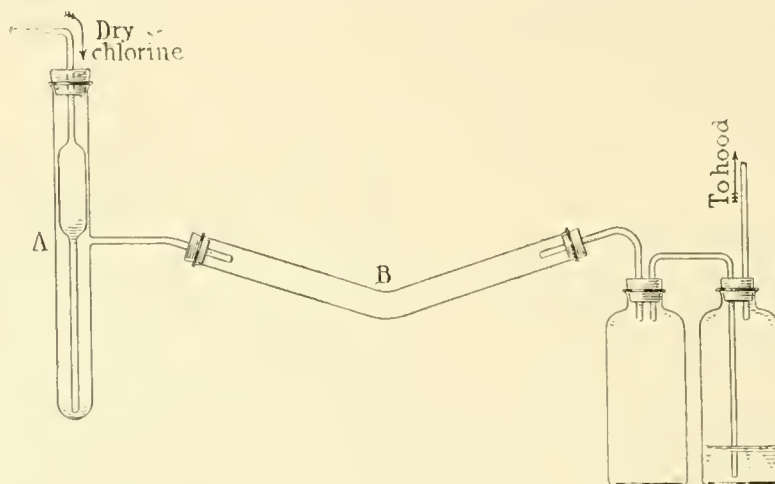


FIG. 1.

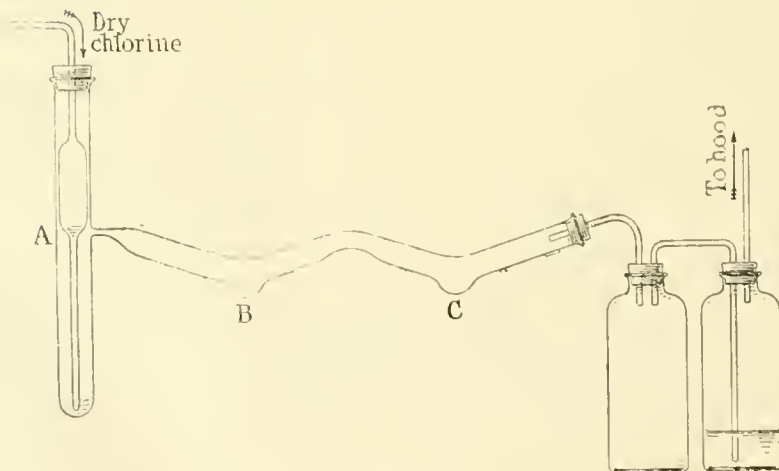


FIG. 2.

[acts warranted the study of the fractional distillation of the anhydrous chlorides] of zinc, indium, and gallium,

* This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by J. Allington Bridgman in partial fulfilment of the requirements for the degree of Doctor of Philosophy. From the *Journal of the American Chemical Society*, xl., No. 10.

reaction between the alloy and the chlorine. The heat of reaction then suffices to complete the chlorination, and it causes some of the chloride to distil to the upper portion of the tube, nearly to the side-arm. After chlorination was complete a Snowdon electric furnace was brought up around the tube A, and this was then heated to about 230° (Cornell Chemist, 1914, iv., 13). This caused a portion

of the chlorides to distil over into B. The temperature was raised to 250° , and the distillation was continued for about one hour. The spark spectrum of the material that condensed in B showed the presence of a preponderating amount of gallium, and the lines of indium were only faintly visible. The material remaining in the tube A showed strong lines of gallium, indium, and zinc.

Purified gallium chloride from the tube B (Fig. 1) was again distilled in chlorine, the side-arm for the apparatus in this case being fused to a tube of Jena glass that had two depressions, B C (Fig. 2). Gallium chloride was

These distillations were carried out in a tube of Pyrex glass of about 20 mm. external diameter, bent into a series of nine depressions (Fig. 3). The tube was constricted between the depressions. 5.3978 grms. of the original alloy was placed in the first bend A, and dried chlorine was conducted through a glass tube, the end of which dipped below the surface of the alloy. The reaction between the chlorine and alloy was started by heating the latter with a Bunsen flame. The action was at first violent, the union of the chlorine with the metals being accompanied by the emission of a bluish light and a play of incandescent

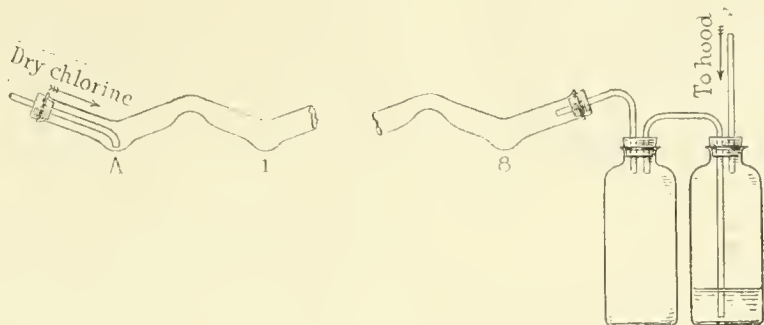


FIG. 3.

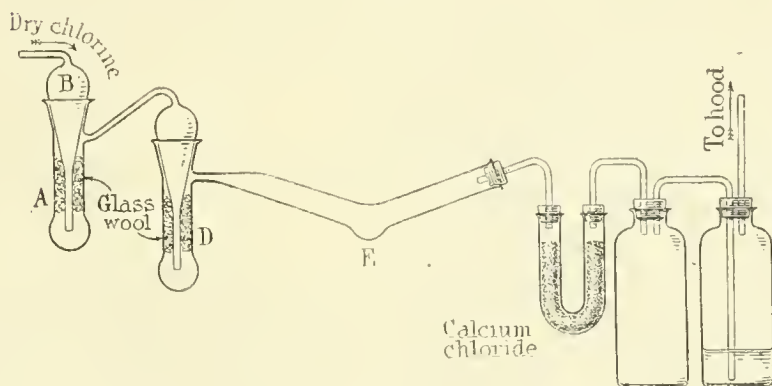


FIG. 4.

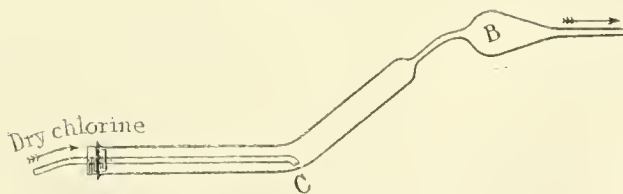


FIG. 5.

melted and poured into the tube A. Dry chlorine was passed through the apparatus, and A was heated to from $220-240^{\circ}$ in a Snowdon furnace. Gallium chloride that condensed in B was then distilled over into the depression C by heating the tube B with the flame of a Bunsen burner. The spark spectrum of the chloride that condensed in C showed very faintly the α -line of the indium spectrum when a large amount of the material was placed in the spark cup.

The above preliminary experiments gave reason to suppose that several successive distillations of gallium chloride in a current of chlorine would free it from indium and zinc.

particles throughout the tube in the neighbourhood of the sample. When a layer of the molten chloride had formed above the metal the chlorination proceeded quietly.

After the metals in the alloy had been completely converted to chlorides, the portion of the tube marked A was surrounded by the asbestos oven mentioned above and was heated from $220-250^{\circ}$. A portion of the chlorides distilled over into depression 1. The chloride was successively distilled in this manner from one section to the next until it finally was collected in the last section, No. 8, of the tube. The distillation of the chloride from one depression to the next was effected by slipping over the

glass tube the barrel of a porous cup from which the bottom had been cut off, and which had been wrapped with nichrome ribbon so that it could be electrically heated. This heating tube was about 7 cm. in diameter and 15 cm. long. In distilling the chloride from section 1 to section 2 the heating tube was placed around depression 1, and the current was adjusted to raise the temperature to 254° . In the succeeding distillations the heating tube was moved along until it covered the section containing the chloride and the current was adjusted to give a temperature ranging from 235 – 245° . A slow current of chlorine was passed through the tube during the distillations. The spark spectrum of the material which condensed in section 8 of the tube, and which consisted chiefly of gallium chloride, still showed faintly the lines of indium and zinc. The indium spectrum was stronger than from the material obtained in the preceding experiment.

The failure to obtain pure gallium chloride by these eight distillations may have been due either to (1) insufficient vertical rise between the different depressions in the distilling tube, which might allow the chlorides of zinc and indium to be carried along mechanically; or to (2) over heating during the chlorination of the alloy, which might cause either the distillation of some zinc chloride, or the distillation of indium monochloride or indium dichloride before the conversion of the indium to the trichloride was complete; these lower chlorides of indium would first be formed, and they are more volatile than the trichloride.

To remove the first of these possible difficulties an apparatus of different form was constructed (Fig. 4). This was blown entirely of Jena glass, and the tubes A and D were fitted at the top with widened inlet tubes that were ground into the necks of the two distilling tubes. The gallium chloride from the two preceding experiments, which was nearly free from zinc and indium, was melted and poured into the tube A. Glass-wool that had previously been washed with hydrochloric acid and carefully dried was inserted in A and D around the inlet tubes. The chlorides were distilled from A into D in a current of dry chlorine by heating A with a Snowdon furnace from 230 – 255° . The material that condensed in D showed the lines of neither zinc nor indium. This chloride was removed from D, dissolved in water, and its solution was electrolysed with a rotating rod of platinum as cathode until a small amount of metal was deposited. The spark spectrum of the solution of this deposit in hydrochloric acid showed the lines of neither zinc nor indium.

Because of the success of this method of distillation in freeing gallium chloride from indium and zinc it was decided to convert the large amount of metallic gallium that had been prepared by electrolysis (see *ante*) to the chloride, and to subject this chloride to all distillations. This gallium was nearly free from indium and zinc. The chlorination of the metallic gallium was carried out in the bent tube C (Fig. 5) of Jena glass that was fused to the inlet tube B of the flask A (Fig. 4). Metallic gallium was placed at the depression C and the chlorination was made as described above, B not being connected with A during the procedure. This avoided the possibility of the distillation of zinc chloride and lower chlorides of indium into A and D during the chlorination of the metal. After chlorination was complete the tube B was inserted into the neck of the flask A, and C was warmed to such a temperature as caused the chlorides to melt and flow down into A. The current of chlorine was continued through the apparatus, and A was heated in a Snowdon furnace while the chloride distilled through the glass-wool from A into D. When all of the chlorides had condensed in D the heating of A was discontinued, and the furnace was brought up around the tube D and the chloride was again distilled through the glass-wool into the tube E, where it condensed.

In the first chlorination and double distillation 5.009 grms. of the purified metallic gallium was employed. A slight leakage of the vapour of gallium chloride into the outer air took place through the ground joints at the top

of A and D. This was stopped in the next distillation by sealing these joints with water-glass.

A second portion of gallium weighing 9.2982 grms. was chlorinated and distilled, and then a third sample weighing 8.4075 grms. was later chlorinated and distilled.

The residue left in A after the first two samples had been distilled over was tested for the presence of zinc with the microscope, using solid potassium mercuric thiocyanate (Behrens, *Zeit. Anal. Chem.*, 1891, xxx., 141), and zinc was found to be present.

The residue remaining in C where the chlorination was carried on and the chloride that condensed in D gave no test for zinc by this method. This method, however, has been found to be not wholly reliable for the detection of minute amounts of zinc in the presence of large amounts of gallium (Ruth E. Chipman, "The Mercuric Sulphocyanates as Reagents in Microscopic Qualitative Analysis," a thesis presented to the Faculty of the Graduate School of Cornell University, June, 1917).

In an attempt to increase the delicacy of this microscopical test for zinc the gallium chloride was first volatilised at 250° and the test was then applied to the residue, but the results were not successful. The most satisfactory method for determining the purity of the gallium chloride prepared by the above method was found to be the photographing of the arc spectrum of the material (see *ante*). This redistilled gallium chloride was found to be spectroscopically free from zinc and indium, and by the method above described it was shown that it could not contain more than 0.005 per cent of either of these two elements. Two successive distillations of gallium chloride in the apparatus shown in Fig. 3 therefore yield a product of high purity.

(To be continued).

THE ESTIMATION OF PHOSPHORUS IN THE PRESENCE OF TUNGSTEN.*

By G. WATSON GRAY and JAMES SMITH (Liverpool).

IN view of the large amount of tungsten used in the manufacture of high-speed steel, the question of the estimation of phosphorus in the presence of tungsten is an important one, but, although important, does not appear to have had the attention it deserves. Judging from numerous analyses which have come under the authors' notice, many chemists seem to find less phosphorus than is actually present. On investigating the cause of some of the low results they were found due to faulty methods. Taking ferro-tungsten as an example, the authors found that the method adopted by many chemists was to decompose the ferro-tungsten by fusion or other methods, separate the tungstic acid by evaporating to dryness with hydrochloric acid, and estimate the phosphorus in the filtrate. This method is altogether wrong, as a large amount of the phosphorus present is precipitated with the tungstic acid as phospho-tungstic acid, and the phosphorus so precipitated is lost. Most ferro-tungstens contain only 0.015 to 0.030 per cent phosphorus, and with these the error is perhaps not quite so glaring, but odd samples made from phosphoric tungsten ores contain up to 0.100 per cent, and sometimes even more. It is in these high phosphoric samples that the error stands out prominently. The authors have seen samples containing 0.100 per cent phosphorus returned as containing 0.020 per cent. To illustrate this point a table of results obtained by using the faulty method described above is given, together with the figures obtained by further examining the residue of tungstic acid for phosphorus. These results are only a few selected from a large number of samples examined.

* A paper read before the Iron and Steel Institute, May 8, 1919.

Sample No.	1.	2.	3.	4.	5.	6.
	P.c.	P.c.	P.c.	P.c.	P.c.	P.c.
Phosphorus in fil- trate	0.023	0.017	0.022	0.014	0.017	0.013
Phosphorus in tung- stic acid residue..	0.057	0.071	0.080	0.055	0.032	0.020
Total phosphorus ..	0.080	0.088	0.102	0.069	0.049	0.033

From the above table it will be seen that the larger proportion of the phosphorus contained in ferro-tungsten is precipitated with the tungstic acid, and any method of analysis which is based on separating the tungstic acid before estimating the phosphorus must give low results for phosphorus. It occurred to the authors that there might possibly be some definite ratio between the amount of phosphorus precipitated and the amount not precipitated, but after making numerous analyses of samples of ferro-tungsten it was concluded that there was no ratio, neither have they been able to determine the conditions necessary either to precipitate all the phosphorus with the tungstic acid or to precipitate the tungstic acid free from phosphorus. These low phosphorus results not only occur with ferro-tungsten, but also with tungsten ores. To quote one example out of many, a sample of wolfram which contained 0.200 per cent phosphorus was returned by one chemist as containing 0.030 per cent. The same state of things also obtains to some extent with tungsten steels—in fact, some tungsten steels when analysed by the usual method show only a trace or no phosphorus at all, even when it is known that phosphorus is present. Indeed, it has been suggested that the phosphorus is slagged out in making tungsten steel because the amount of phosphorus in the ingredients used was so much higher than that found in the finished steel. It appears to the authors that the discrepancy is due not to slagging out the phosphorus, but to the whole of the phosphorus in the finished steel not being obtained in the analysis owing to the cause stated above.

The method devised by the authors for the estimation of phosphorus in ferro-tungsten, tungsten powder, and tungsten ores, which has proved to be an accurate one after some years of service, is as follows:—

Fuse 2 grms. of the finely powdered sample with 10 grms. nitre mixture ($\text{Na}_2\text{CO}_3 + \text{KNO}_3$ in molecular proportions) in a large covered platinum crucible, dissolve the melt in the least possible quantity of water, filter, and wash free from tungstates with boiling water containing a little ammonium nitrate (six washings are sufficient). Ignite the residue in the original crucible, transfer to a 400 cc. beaker, dissolve in hydrochloric acid, and evaporate to dryness. To the filtrate add 20 cc. hydrochloric acid, and about 2 cc. bromine (bromine, not bromine water), stir well until the liquid is distinctly coloured by bromine, add ammonia until the precipitated tungstic acid is dissolved, and then a further quantity of strong ammonia equal to one-fourth of the original bulk of the liquid. The volume of the liquid should now be about 250 cc. Cool and add 3 cc. magnesia mixture, stir well, and allow to stand for six hours, or preferably over night. It is generally supposed that ammonium magnesium phosphate is much more soluble than it really is. The authors found that under the conditions described, the phosphorus is completely precipitated by magnesia mixture.

Filter through double papers and wash six times with ammonia water (10 per cent). Dissolve the precipitate in hydrochloric acid, allowing the liquid to run into the beaker containing the iron, evaporate to dryness, take up with 10 cc. hydrochloric acid, dilute, saturate with sulphuretted hydrogen to remove arsenic, tin, &c.; filter, wash, boil off sulphuretted hydrogen, add 50 cc. ferric chloride (1 gm. pure iron dissolved in hydrochloric acid, oxidised with nitric acid, and made up to 1 litre), cool completely, add ammonia until a distinct dirty green precipitate is obtained, then acetic acid until the precipitated ferrous hydrate is dissolved, boil well, and filter off the basic ferric acetate which contains all the phosphorus,

dissolve in hydrochloric acid, boil, add a few cubic centimetres nitric acid, and precipitate with ammonia. Boil, filter, wash, dissolve in nitric acid, and precipitate the phosphoric acid with ammonium molybdate as usual.

The method may also be used for the estimation of phosphorus in alloy steel, but as steel cannot be fused directly with nitre mixture it should be dissolved in nitric acid in a dish or wide beaker, evaporated to dryness, and baked on a hot plate until the nitrate of iron is decomposed to oxide. The resulting oxide of iron, &c., can then be easily and cleanly removed from the dish or beaker with the aid of a flexible spatula and wiping with a little damp filter paper. It is then fused with nitre mixture and the analysis proceeded with as directed for ferro-tungsten. The method is especially useful for vanadium steels, as by its means the vanadium (which interferes very considerably with the estimation of phosphorus by the molybdate method) is completely got rid of before precipitating with molybdate.

The authors have submitted the method to chemists in several large steelworks, who have found it satisfactory.

CHLORINATION OF BENZENE.

At a meeting of the Birmingham and Midland Section of the Society of Chemical Industry on Tuesday, May 6 (Dr. E. W. Smith presiding) a paper on the "Chlorination of Benzene—Analysis of Mixtures of Benzene, Chlorobenzene, and Dichlorobenzene, &c.," was read by Mr. S. Raymond Carter, who had prepared the notes with the aid of Percy F. Frankland and Dorothy Webster.

This method is similar in principle to that employed by H. G. Colman for the determination of toluene in commercial toluol, and consists in distilling from an Engler flask 100 cc. of the sample at the rate of 7 cc. per minute and interrupting the distillation at 122°C . (corr.) and 142°C . (corr.). From the amounts distilling below 122° and above 142° the percentages of benzene and chlorobenzene are obtained from a graph, and the dichlorobenzene may be found by difference.

Experiments with mixtures of known composition have shown that the percentages of benzene and chlorobenzene deduced from the graph are not affected by the other products which are likely to be formed during the chlorination of benzene. The method is an expeditious one—a distillation being complete in half to three-quarters of an hour, and it proves eminently suitable for investigating the products obtained from the chlorination of benzene either on the experimental or industrial scale.

INTER-ALLIED CONFERENCE OF CHEMISTRY AT PARIS.

ON the initiative of the Société de Chimie Industrielle an inter-allied conference has recently been held in Paris. The French delegates included representatives of the Société Chimique de France, the oldest French chemical society, the Société de Chimie Industrielle, l'Association des Chimistes de Sucrerie et Distillerie, the Société de Chimie Physique, the Société de Chimie Biologique, the Société des Experts Chimistes, l'Association des Chimistes de l'Industrie Textile. Belgium was represented by M. Chavanne; the United States by Mr. Wigglesworth, Dr. Cottrell, Lieut.-Col. Barton, Mr. John Pennie, Lieut.-Col. Zanetti, Lieut.-Col. Norris, Major Colin Mackall, Lieut. Sidney Kirkpatrick, and Mr. Donald Riley; the United Kingdom by Sir William Pope, Prof. Henry Louis, Mr. Chapman, Mr. Reid, Mr. Stephen Miall, Mr. Edwin Thompson; Italy by Prof. Emanuel Paterno, MM. Giuseppe Paterno, Pomilio, Giordani, Parodi-Delfino, and Barbier. Prof. Charles Moureu presided over the meetings,

which took place in private, and at which the statutes of an international confederation, which is to aim at bringing about an intimate alliance between France, England, Belgium, the United States, and Italy, were fixed. An inter-allied council, which is to meet in London on July 15-18, was appointed, each nation appointing two members as follows:—

Belgium—MM. Chavanne and Crismer.
United States—Dr. Cottrell and Lieut.-Col. Zanetti.
France—MM. Meureu and Paul Kestner.
Great Britain—Sir William Pope and Mr. Henry Louis.
Italy—Senator Paterno and M. Parodi-Delfino.
General Secretary—Mr. Jean Gerard.

At the public meetings, which took place on April 14 and 15, communications of the greatest interest were presented. Prof. Louis described modern methods of enriching iron minerals by magnetic separation, and Dr. Cottrell gave an account of the preparation of helium for balloons and dirigibles. A communication on the potash industry in the United States by Mr. MacDowell was also read at the meeting on April 14, and on the following day an exposition of the American patent laws was given by M. John Pennie. A banquet was held in the evening, and on the 16th a visit was paid by the members of the Conference to the devastated region of Chauny.

BOARD OF TRADE ANNOUNCEMENTS.

IMPORT RESTRICTIONS

THE President of the Board of Trade, after duly considering the recommendations of the Consultative Council on Imports, has given the following further directions in regard to the prohibitions of imports:—

The restrictions on the importation of the following articles are to be removed.

201. Printing inks.
202. Oil-lamp burners.
203. Gas-burners.
204. Metal parts and accessories of pedal cycles except those mentioned under No. 225.
205. The following painters' colours and pigments except in so far as they may fall within the scope of the Prohibition of Import (No. 29) Proclamation of February 24, 1919:—Asphaltum; bitumen for black varnish; bone pitch; Brunswick black; burnt sienna; bone black; carbon black; carmine; China ink; Chinese ink; cinnabar native; cobalt oxide; earth colours; earth sienna; gamboge; gamboge gum; Indian ink; imitation gold leaf; lime green; ochre; orpiment; umber; zaffre.
206. Aluminium powder.
207. Fancy goods (articles de Paris).
208. Jewellers' findings; that is, chain, brooch catches, pins and joints, snaps, bolt and split rings of base metal or gilt.
209. Paints and enamels (from July 1).
210. Aerated mineral and table waters.
226. The following painters' colours:—Litharge, ultramarine blue, white lead, satin white, lamp black.
227. Metal fittings and frames for bags and trunks.
228. Raw spirits for industrial purposes.
229. Reclaimed rubber.

In accordance with the above, general licences have been issued for the articles mentioned in items 202 to 206. In the case of printing inks and aerated mineral and table waters general licences are already in operation, and a general licence will be issued in due course for paints and enamels.

Applications for special licences should be made as usual to the Department of Import Restrictions, 22, Carlisle Place, London, S.W. 1.

EXPORT OF FOODSTUFFS TO GERMANY.

The Board of Trade announce that, following on the relaxations recently made in the Blockade regulations relating to foodstuffs whereby:—

- (a) The quantitative limitations on the import of foodstuffs into neutral countries have been removed;
- (b) Consignment may be made direct to neutral traders, and need no longer be made through the N.O.T. or other importing associations; and
- (c) Export from neutral countries to Germany is allowed;

it has been decided to authorise the resumption, by firms in the United Kingdom, of exports of foodstuffs to Germany, through neutral and allied countries, within the monthly ration of foodstuffs allowed to Germany under the Brussels Agreement, and a general licence under the Trading with the Enemy legislation has been issued to give effect to this decision.

All arrangements for finance should be made by, and at the risk of, the private traders and the neutral or allied firm or Government concerned.

Foodstuffs on List C of prohibited exports may be exported to Northern Neutrals and Switzerland, as well as to allied countries without licence; but foodstuffs on Lists A and B can be so exported only under licence from the Export Licence Department, 4, Central Buildings, S.W. 1.

The term "Foodstuffs" means food, beverages, spices, edible oils, or other articles intended solely for the manufacture of human food.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, May 15, 1919.

Sir J. J. THOMSON, O.M., President, in the Chair.

THE following papers were read:—

"On the Area of Surfaces." By Prof. W. H. YOUNG, F.R.S.

Many attempts by well-known writers have been made to frame a theory of the area of surfaces. These efforts have been attended with so little success that even the most recent text-books define the area of a curved surface by means of the formula known to hold in the case of a surface of revolution. Not even in the matter of the definition itself has anything which can be regarded as final been achieved, still less has it been found feasible to proceed from the definitions which have been given to the formula required.

In the present communication the author attacks the question from an entirely new point of view. The definition given is based on what is itself a new concept, namely, that of the area of a closed skew curve. It is characterised further by the use to which is put the idea that the surface is, like a curve, an ordered manifold, the order being double instead of single.

The surface is accordingly supposed defined by equations of the form—

$$x = x(u, v) \quad y = y(u, v) \quad t = t(u, v)$$

and divided up by the curves—

$$u = \text{const.} \quad v = \text{const.}$$

On the fact that the sum of the areas of the boundaries of the portions of surface thus obtained has a unique limit, the definition of the area of a surface is based. The curve boundaries have in fact an area whenever they possess a length. Moreover, the unique limit obtained for their sum is shown under very general conditions to have precisely the value given by the well-known formula.

It may be added, though this is not proved in the paper, that the theory developed may be utilised to indicate the limitations of the older method, based on triangulation, and at the same time to notably extend such results as have been obtained by earlier writers.

"On Change of the Independent Variables in a Multiple Integral." By Prof. W. H. YOUNG, F.R.S.

"Researches on the Chemistry of Coal. Part I. The Action of Pyridine upon the Coal Substance." By Prof. W. A. BONE, F.R.S., and R. J. SARJANT.

The paper records the result of an experimental investigation of the so-called solvent action of pyridine and homologues upon the coal substance, with the double object of clearing up certain discrepancies in the work of previous investigators, and of determining the real nature of the action in question.

It is shown that the presence of oxygen has an important retarding action upon the extraction process (the extent of which varies considerably with the nature of the coal), and that in order to obtain consistent results in any such process, it is necessary not only to employ an anhydrous solvent, but also to exclude oxygen. A suitable apparatus and method are described for carrying out the process under standard conditions, such as will give consistent results of comparative value with various coals.

The application of the method to two typical isomeric bituminous coals is fully described. It is shown that when such extraction is carried out at ordinary pressures, with exclusion of oxygen, a practical limit is finally attained. In the case of the two coals in question, this limit considerably exceeded the amount of "volatiles" yielded by them on carbonisation at 950°. At higher pressures this first limit was considerably passed, and when conducted in sealed tubes between 130° and 150° as much as two-thirds of the coal substance was rendered soluble.

The results as a whole indicate that neither pyridine alone, nor even pyridine in conjunction with chloroform, is capable of extracting in a pure condition the resinic constituents of the coal substance, and that in addition to any ordinary solvent action which pyridine may have upon such constituents it also at the same time slowly attacks and resolves into simpler molecular aggregates the complex structure of the coal substance as a whole, for which it has a marked affinity.

"A New Method of Weighing Colloidal Particles." By Prof. E. F. BURTON.

When fine colloidal particles are dragged up and down for equal periods in a liquid by the application of a vertical electrical field a net settling of the particles is noted. It is thought that, although for small forces such as gravity alone the Brownian movement prevents the attainment of any limiting velocity, yet when the particles are dragged by a much larger force the comparatively insignificant gravitational force is added to the electrical for downward motion and subtracted for upward motion, thus becoming effective in producing a net settling of the particles.

Application of Stokes's Law to this net settling gives a value for the size of the particles very closely agreeing with that obtained by the counting method (e.g., 2.2×10^{-5} cm. and 1.7×10^{-5} cm.) even though values to hand are taken from old observations made when this net settling was not appreciated and not closely observed.

Experiments are now in hand to determine this settling very exactly. By the application of ultra-microscopic illumination of single particles in a slowly alternating field, it is hoped that the setting will be observed over an extended interval and that a very exact method of weighing these particles will be developed. In addition, the method should prove useful in determining the effect of the addition of various electrolytes on the size of colloidal particles and thereby shed much light on incipient processes of coagulation.

"The Value of the Rydberg Constant for Spectral Series." By W. E. CURTIS.

PHYSICAL SOCIETY.

Ordinary Meeting, March 28, 1919.

Prof. C. H. LEES, President, in the Chair.

A DISCUSSION ON "*Metrology in the Industries*" was held.

SIR RICHARD GLAZEBROOK, C.B., F.R.S., in opening the discussion, traced briefly the early history of metrology. While in some form or other it must have been employed in the very earliest times—if what antiquarians told us of the Pyramids was correct—the first application of really accurate measurement to mechanical engineering was chiefly due to Sir Joseph Whitworth, who taught people to make their length measurements with great accuracy and introduced reference gauges. The next step was the use of limit gauges. This greatly simplified the gauging of repetition work. At the time of the Boer War the supplies of ammunition, especially breech plugs of guns, were not interchangeable as obtained from different shops. This led to the formation of the Engineering Standards Committee on Gauges, which tackled the problem of producing accurate gauges with defined limits and tolerance, and by 1914 a certain number of firms had introduced the use of limit gauges. In 1915 the cry for munitions on a great scale brought home the great importance of interchangeability and the need for strict standardisation of gauges. When screw gauges were first tested at the National Physical Laboratory the rejections totalled 75 to 80 per cent; but after two years this was reduced to about 20 per cent. Now, if we are to maintain our position in peace, the maintenance of interchangeability in the engineering manufacture is equally necessary, so that we may manufacture in quantity. Much has yet to be done if we are to keep ahead, and the co-ordination of research with routine testings is vital to the progress of the science.

MR. TAYLOR (of Messrs. Taylor, Taylor, and Hobson) agreed that the war had produced a great advancement in the standardisation of manufactures; but we were apt to overlook much that had been done in this way before the war. Interchangeability of manufacture had existed, for instance, in the watch trade in Switzerland for centuries. In America, interchangeable manufacture had been introduced by Col. Colt in the Civil War, and was widely practised in America before it was generally understood in this country. But something, nevertheless, had been done in this country. The Linotype Company had done much in this way, while bicycle making had taught us a great deal of interchangeable manufacture. Our schools were at fault in teaching the science of design to the exclusion of the science of the workshop.

SIR HENRY FOWLER (Chief Mechanical Engineering Department, Midland Railway) said he was sure the country did not realise the debt it owed to the National Physical Laboratory in connection with gauges. While, as Mr. Taylor had said, a certain amount of interchangeable work was done in this country before the war, the country, as a whole, did not appreciate the advantage of limit gauges. A great deal of education is still wanted. To produce economically we must produce in quantity. For this it is essential to have interchangeability, and we can only have this if the science of metrology goes ahead.

DR. P. E. SHAW (University College, Nottingham) said he thought the extent to which metrology had now permeated the workshops of the country made decentralisation desirable, and he thought the universities were the proper sites for the subject. He had instituted a department of metrology in University College, Nottingham, in 1916. The instruction would be mainly practical, but preliminary lectures would be necessary as well. In addition to the instruction work testing should be done, the standards used being verified periodically at the National Physical Laboratory. Such work is essential to the vigorous growth of the subject.

Mr. DYKES emphasised the importance of limit gauges in all classes of manufacture, even of such things as ploughshares and perambulator wheels. He recommended that the National Physical Laboratory should have two classes of tolerances for commercial gauges, the lower class being suitable for coarser work. He urged the more widespread use of the screw gauge protector.

Mr. M. F. RYAN (Director of Munition Gauges) said the early production of gauges was seriously hindered by the measurements on the standards from which the drawings were being made being inaccurate, so that gauges correctly made to the drawings might not fit the standards. When the National Physical Laboratory took over the testing this state of affairs was quickly exposed. The work of teaching the manufacturers was also carried out by the N.P.L., and it is largely due to this that the large output (10,000 per week before the armistice) was secured. He was heartily in favour of Dr. Shaw's suggestion of setting up a metrology department in the universities.

Mr. J. E. SEARS (Supt. Metrology Dept., National Physical Laboratory) said the intimate association with manufacturers of gauges and also of the products for which the gauges were intended, had given them an opportunity during the war of attaining quite exceptional progress in the subject. He thought limit gauge work was going to be an important factor in all future engineering; and, if interchangeability between the work of different firms had to be maintained, it is evident that all the controls of such gauges must be referred to a central authority governing the fundamental standards of length. It was essential that the Laboratory should also have a fair amount of test work in order to maintain the close contact with the manufacturers that had proved so useful in the past. There would still, of course, be plenty of work for local centres, which he agreed were desirable; but he did not think the universities were the most suitable places for such work to be carried out.

Mr. W. H. BOLTON (University of Sheffield) emphasised that education was necessary among manufacturers before they would realise that standardisation was essential to efficiency in their business. In Sheffield one firm made 1700 different patterns of pocket knife. He thought a scheme of decentralisation was vital to the nation, and he disagreed with Mr. Sears as regards the relation of the universities to test work. He regarded test work as essential if these institutions were to keep in touch with industrial requirements.

Mr. B. P. DUDGING (of the National Physical Laboratory) said that in nearly every case when one comes to apply measuring to a specific problem one has to conduct some researches as to how the measurements should be made, what instrument to use, and how to use the instrument. The research worker needs to have a good workshop behind him.

Sir RICHARD GLAZEBROOK, in replying to the discussion, expressed his satisfaction at the interest in the subject which was evidently springing up all over the country.

The PRESIDENT, in closing the meeting, said that several points of importance were brought out prominently throughout the discussion. These were first, that under the stress of the war many manufacturers have learned to use limit gauges with very great improvement to their work. Second, that there is a tendency to slip back into old methods, which must be vigorously resisted. Third, that sub-stations where accurate testing could be carried out locally, in close association with the National Physical Laboratory, were essential to the future development of metrology.

An exhibit of Optical Scales and Graticules, by Mr. J. Rheinberg, was on view at the close of the meeting.

BLACK VARNISH FOR WOOD can be made by dissolving bitumen in carbon bisulphide. If the odour is objected to, carbon tetrachloride can be used instead of bisulphide.

NOTICES OF BOOKS.

Applied Optics: The Computation of Optical Systems. Being the "Handbuch der Angewandten Optik" of Dr. ADOLPH STEINHEIL and Dr. ERNEST VOIT. Translated and Edited by JAMES WEIR FRENCH, B.Sc. Glasgow and Bombay: Blackie and Son, Ltd. Two Volumes. Price 12s. 6d. net each.

The present work, an edited translation from the Standard German work of Steinheil and Voit, is issued with the approval of the Standing Committee on Glass and Optical Instruments appointed by the Advisory Council of the Department of Scientific and Industrial Research, in order to provide the British Optical Industry with a handbook presenting a complete Trigonometrical System of Optical Computation in a form suitable for practical use.

Mr. James Weir French, B.Sc., of Messrs. Barr and Stroud, Ltd., who is himself a member of the above Committee, is responsible for this edition in English. Through his wide experience in optical productions he has been able to supply a work that is eminently suited to the practical conditions of the present day. It is thus not a mere translation; it owes much to Mr. French's own specialist knowledge of a highly technical subject.

A distinguishing and essential feature of the original work is the very complete system of symbols and sign convention employed. The portion of the original appendix which deals with this has been included in both volumes. To illustrate the meaning of the symbols there has been added a series of ten diagrams over and above those that appear in the original. These diagrams include examples descriptive of the sign convention.

The diagrams form an important element in the work. To render them abundantly clear they are printed in colours, whereby their convenience for ready reference is greatly increased.

NOTES.

RECENTLY we had had occasion to turn up No. 1 of the CHEMICAL NEWS, published on Saturday, December 10, 1859. It was edited by William Crookes, and the general appearance is much the same as to day's issue. The matter is interesting. The first paper is by C. Grenville Williams on "Vapour Volume," and we read about oxygen with an atomic weight of 8, and are warned that it is safer to adhere to the old notation until further researches have shown its fallacy. The table of contents contains papers on the "Separation of Nickel and Cobalt from Peroxide of Iron" and on "Platinum and its Associated Metals," by MM. Deville and H. Debray. The metal had been introduced into the laboratory but a few years back, and speculations are raised as to its possible uses. The paper is chiefly occupied with the metallurgy of platinum and can be studied with profit to day. A paper by John Spiller, F.C.S., deals with the production of a carbon ink, in which concentrated sulphuric acid, indigo, sugar, and gum are used; the author mentions the need for using a gold or a quill pen, and also the fact that the paper must needs be thick as the written characters penetrate somewhat! In the "Proceedings of Societies" a meeting of the Chemical Society is reported, with B. C. Brodie, F.R.S. in the chair, and we read discussions in which Dr. Hofmann, C. L. Bloxam, Dr. Miller, and Dr. Odling take part. The advertisement pages, too, are interesting; many familiar names appear. James R. Gregory offers collections of minerals; Churchill, Van Voorst, Mitchell, and others offer books. "Elements of Chemistry," by William Allen Miller, is announced as just published. The principal difference between the first issue and that of to-day is the presence in the former of

matter and advertisements dealing with pharmaceutical chemistry and medicines. On reading through the issue it is impossible not to notice the tremendous advance in the chemistry of to-day over that of sixty years ago; an advance that we can confidently assume will continue; so that the subscriber to the *CHEMICAL NEWS* sixty years hence may find as much interest in reading to-day's issue as we do in reading Prof. Bloxam's demonstration at the Chemical Society of the decomposition of ammonia by means of the discharge from a Rühmkorff coil.

THE Second "Report on Colloid Chemistry" has just been published; the first report was issued in 1917 by the British Association for the Advancement of Science, but on account of financial difficulties consequent on the War they were unable to meet the greatly enhanced cost of publication for the Second Report. Under these circumstances, and in view of the importance of the subject, the Department of Scientific and Industrial Research has arranged that this Second Report should be published by H.M. Stationery Office, and it is now on sale at 6d. net. The work occupies some 170 pages and is very complete: historical matter, practical applications, and theory are exhaustively treated, and the publication will be found of very great value in almost all industries.

AUTOMATIC AND ELECTRIC FURNACES, LTD., of 281-283, Gray's Inn Road, W.C. 1, have designed and placed on the market a series of electric muffle furnaces that are likely to become of use in chemical and technical laboratories. They appear to be of simple and robust construction; they are capable of giving temperatures up to 1000° C. and are wound for any voltage between 100 and 250 volts for continuous or alternating current circuits.

IN a paper on "Some Observations on the Use of Boric Acid as a Disinfectant," Fred W. Tanner and Ruth S. Funk (Bacteriological Laboratory, University of Illinois, Urbana, Ill.) give an account of some carefully conducted experiments showing the effect of this agent on a number of bacteria. A saturated solution of boric acid in distilled water was used and tubes of dextrose agar were inoculated and incubated. The result showed that very little if any germicidal action followed the use of even large amounts of boric acid. Further experiments were made using the silk thread method of inoculation, which also gave a very poor result, and the general conclusion of the authors is that the use of this reagent should be discontinued in those cases where disinfection is absolutely essential.

BERI BERI, a disease prevalent in Eastern Asia, has been found to be very common where polished rice was the main article of diet. On treating patients suffering from the disease with extracts from the husks and polishings removed from the rice marked improvements were noted. It appears that the "vitamines" contained in the husks of rice and other grains are very necessary, and their removal may lead to unappetite results.

SIR JOSEPH J. THOMSON, O.M., President of the Royal Society and Master of Trinity College, Cambridge, has been appointed by an Order of Council dated May 8, 1919, to be a member of the Advisory Council to the Committee of the Privy Council for Scientific and Industrial Research.

THE Institute of Chemistry is operating with the Appointments Department of the Ministry of Labour in view of the resettlement in civil life of chemists who have served with the forces. The Council is said to have stated that "Salaries of £300 a year and upwards (with prospects) would command a good selection of candidates." This statement has given rise to some comment on account of the smallness of the minimum suggested, but unfortunately we are in possession of information that shows that salaries of considerably less than this have

been offered and accepted by chemists who, upon demobilisation, have found great difficulty in obtaining appointments.

PIEZO-ELECTRICITY, the production of electricity by pressure upon crystals, although observed many years ago, has only been applied to practical uses of late years. The matter was studied exhaustively by M. Curie, who devised and used an instrument based upon the principle in the early work upon radio-activity that led eventually to the discovery of radium. To M. Curie is due the discovery that the quantity of electricity developed in a crystal by pressure is exactly proportional to the pressure. Sir J. J. Thomson has recently drawn attention to the phenomena in a lecture delivered at the Royal Institution, and suggested the possibility of using it for the measurement of suddenly developed pressures such as are met with in artillery and explosion of gun-cotton, &c. Explosions have been recorded lasting only 1/100,000th sec. The method is likely to find many applications in the near future.

GRANTS FOR SCIENTIFIC RESEARCH IN SOUTH AFRICA.—The Research Grant Board which has been established by the Union Government in South Africa for the encouragement of scientific research, has recently announced its scheme for awarding research scholarships and making grants towards the expenses of scientific research. The scholarships will vary in value from £80 to £250 per annum for one or two years, and may be awarded for a further period. Applications must be made through, and with the approval of, one of the governing bodies of the higher educational institutions of the Union or of a Museum or Research Institute. H.M. Senior Trade Commissioner in South Africa has forwarded the Regulations of the Board, and these may be consulted at the Enquiry Room of the Department of Overseas Trade.—*Board of Trade Journal*.

NOTES FROM FOREIGN SOURCES.

Graphitic Carbon and Graphitic Acid.—V. Köhlschütter and P. Haenni.—By graphitic acid the authors mean the solid oxidation products which are obtained by subjecting pure graphite, prepared electrically, to the action of a mixture of nitric acid, sulphuric acid, and chlorate. It is essential that the oxidising mixture should be taken up by the whole mass of graphite, and that the chemical action should take place simultaneously from the interior. This is brought about by the nitric acid; oxidising agents which do not penetrate into the substance lead only to the simplest oxidation products. When the oxidising action is repeated the proportion of carbon in the product is gradually decreased, and the flakes of graphitic acid dissolve to form reversible colloid products. When dry graphitic acid is heated to 200° carbon separates, water, CO, and CO₂ being simultaneously formed. The carbon thus obtained possesses all the properties of soot, but it can comparatively easily be compressed to give a dense mass of a graphitic nature. Sulphuric acid also decomposes graphitic acid at 160–180°, giving CO and CO₂ in proportions which depend upon the way it is heated. Reducing liquids produce carbonaceous products resembling the original graphite, mixed with by-products of the reaction. The experimental results seem to show that there is no essential difference between amorphous carbon and graphite, and the peculiar properties of the latter are due to a peculiar state of division and dispersion.—*Zeitschrift für Anorganische und Allgemeine Chemie*, 1919, cv., 121.

Cyclisation by Elimination of a Nitro Group.—S. Reich and V. Nicolaeva.—The authors have prepared the oxime of 2,4-dinitroacetophenone by the action of amyl nitrite upon 2,4-dinitroethylbenzene in presence of sodium

alcoholate. When the oxime is heated for a quarter of an hour with 15 per cent hydrochloric acid and water is added, the phenylhydrazone of 2,4-dinitroacetophenone is obtained, and this yields methyl-nitro-indoxazene on the addition of aqueous soda to its alcoholic solution in the cold. The cyclisation takes place with elimination of nitrous acid. Secondary products are also obtained by the reaction, but the authors have not yet studied them. The most abundant product is methyl-nitro-indoxazene, which can be purified by crystallisation in alcohol; it forms yellowish crystals which melt at 114°. —*Bull. Soc. Chim. de France*, 1919, xxv-xxvi., 190.

Action of Alcoholic Potash on Resins.—Paul Nicolardot and Charles Cofiquier.—The authors have studied the action of alcoholic potash on different resins, heating 1 gm. of the resin for an hour with 25 cc. of N/2 alcoholic potash, using a reflux condenser. 50 cc. of water were then added and the insoluble residue was filtered off and weighed. Of the twenty-seven different types of resins examined, all but one left an insoluble substance, and the addition of water enabled them to be classified in three groups:—(i.) Those with which the amount of insoluble product was unaffected by the addition of water; (ii.) those with which the addition of water led to the total or partial disappearance of the insoluble part; (iii.) those which showed an increase of the insoluble part when water was added. It appears that the action of alcoholic potash gives rise to resinous soaps, some of which are more soluble in alcoholic potash than in water, while others, on the contrary, are more soluble in water than in alcoholic potash. It is possible that this new characteristic may be employed in the identification of different resins. —*Bull. Soc. Chim. de France*, 1919, xxv-xxvi., 200.

Mobility of Hydrogen Atoms in Organic Molecules.
Action of Phenyl Hydrazine on Dioxindols.—J. Martinet.—Among the factors which may influence the mobility of hydrogen atoms two are specially important—the neighbourhood of electro-negative elements and a particular position with regard to double bonds. If two atoms α and β are united by a single bond an atom of hydrogen attached to α is mobile if β has a double bond. In dioxindol one atom of hydrogen is thus placed, while another is united to an atom of oxygen. Hence, although the carbonyl group of the dioxindols has a lactamic and not ketonic character, the structure of these substances recalls that of the α ketonic alcohols, which with phenyl hydrazine give diphenyl hydrazones or osazones. If the readiness of the secondary alcoholic function to undergo oxidation is due to its position with regard to the double bond of the ketonic group, a similar action on dioxindol might be foreseen, one molecule of phenyl hydrazine acting as oxidising agent, while a second entered into combination. Experiment has confirmed this hypothesis, which the authors have verified in the case of dioxindol and five of its homologues chosen from different groups. The reaction must be carried out in an atmosphere of hydrogen, and various media, such as water, alcohol, acetic acid, or mixtures of these three, were tried. In all cases the reactions were practically instantaneous at the boiling-point of the solvent and the yields were good. —*Comptes Rendus*, 1919, clxviii., 689.

Reaction of Aconitine.—L. P. J. Palet.—Dragendorff has stated that a characteristic reaction of aconitine is the formation of a reddish coloration when it is heated with phosphoric acid. Other observers have failed to obtain this coloration or have noticed it only with impure specimens, such as the aconitine obtained from the organs of animals poisoned by this alkaloid, which might be explained by supposing that it was due to the presence of a decomposition product. The author has obtained positive results with two samples of amorphous aconitine, using concentrated phosphoric acid and heating directly over a small flame until fumes were given off. A violet coloration was thus produced, while with crystallised specimens only a greyish colour was obtained, as Barthe

has previously stated. If the reagent employed is a mixture of phosphoric acid and sodium molybdate, in the proportions of 25 to 1 by weight, a very intense violet coloration is obtained even with crystallised specimens which were unaffected by phosphoric acid alone. Many other products, such as apomorphine, atropine, brucine, cocaine, &c., were tested similarly, and although they gave various colorations the only ones which could be confused with those obtained with aconitine were aspidospermine and veratrine. These, however, can readily be distinguished from aconitine by trying the effect of oxidising agents on the first and on mineral acids upon the second. —*Journal de Pharmacie et de Chimie*, 1919, x'x., 295.

Action of Phenyl Magnesium Bromide upon the Polyhalogen Derivatives of Ethane. Fred Svaris.—The author endeavoured to obtain fluorystyrene by the action of phenyl magnesium bromide upon difluorodibromethane, expecting to get difluorobromomethyl benzene which, with alcoholic potash, would yield difluorystyrene. But the products actually obtained were difluorethylene and brombenzene. Thus the magnesium compound acted as a reducing agent, removing two atoms of bromine. Various polyhalogen derivatives of ethane were then submitted to the action of phenyl magnesium bromide, and it was found that the principal reaction with bromine derivatives was the subtraction of two atoms of halogen, with the production of brombenzene and an ethylenic derivative. When an atom of carbon was united with fluorine and bromine the latter was removed. With chlorine derivatives a molecule of hydrazine was removed, and this reacted with the magnesium compound to give benzene. In many cases magnesium fluoride was obtained, but was present in a colloidal state. Various secondary reactions also took place, diphenyl being frequently formed, especially in the case of reactions which take place slowly.

MEETINGS FOR THE WEEK.

Monday, June 2.

Royal Institution, 5. (General Meeting).
Royal Geographical, 5.30. (Anniversary Meeting).

Tuesday, June 3.

Royal Institution, 3. "Listening under Water," by Prof. W. H. Bragg.
Institution of Electrical Engineers, 6. "Continuous Wave Plant at the Carnarvon Station," by Senatore G. Marconi.
Röntgen Society, 8.15. (Annual Meeting).

Wednesday, June 4.

Society of Public Analysts, 8. "Examination of Commercial Samples of Nicotine," by Percival J. Fryer.
"Mexican Insects in Poultry Food (Notonecta, Corixa, and Mexican Cantharides)," by T. E. Wallis.
"A Rapid Method for Determining Nickel and Cobalt in Ores and Alloys.—Part. III.," by W. R. Schoeller and A. R. Powell.
"Notes on the Oil of Ceratotheca sesamoides," by E. Richards Bolton.
"An Improved Method for the Estimation of Nitrates in Water by means of the Phenolsulphonic Acid Reaction," by Robert C. Frederick.
"Estimation of Morphine in Indian Opium," by Jitendra Nath Rakshit and Frank J. D'Costa.

Thursday, June 5.

Royal Institution, 3. "The Balkans," by Sir Valentine Chirol.
Royal Society of Arts, 5.30. "Aviation as Affecting India," by Brigadier-General Lord Montagu of Beaulieu.

Friday, June 6.

Royal Institution, 5.30. "Atomic Projectiles and their Collisions with Light Atoms," by Prof. Sir Ernest Rutherford.

Saturday, June 7.

Royal Institution, 3. "The Italian Front," by J. M. Price.

THE CHEMICAL NEWS

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THEORY OF ALLOTPROPY: ALLOTPROPES AND ALLOTPROPOIDS

By MAURICE COPISAROW.

THE term *allotropy* was first introduced by Berzelius (*Fahresb.*, 1841, xx., 11, 13) as denoting the appearance in several states, distinguished from each other by different properties, a definition lacking in precision, owing to the numerous possible interpretations of the "different properties." This vagueness is put forward as a guiding principle by Lothar Meyer (Watts' "Dictionary of Chemistry," 1888, i., 128), who considers that the notion of allotropy is not to be defined with perfect exactness.

Allotropy is taken as a term covering the different physical states of matter, and also isomerism, polymerism, and polymorphism (Lehmann, "Zeit. Krystal. Min.," 1877, i., 97; Lowry, *Trans. Faraday Soc.*, 1916, ii., 150), and in this sense might appear, perhaps, to be an unnecessary term without exact meaning in chemical nomenclature.

This inclusion of different phenomena, along with Ostwald's and Nernst's definition of allotropy on the basis of energy changes, and Benedick's, Honda's, and Le Chatelier's conception based upon the discontinuity of forms, phases, and properties, is due to the consideration of effects of instead of causes underlying phenomena.

Whilst the close study of various properties of matter consequent to a certain phenomenon may help us in comprehending the phenomenon itself and its relation to other natural manifestations, it is wrong to define a phenomenon by its effects, especially when these effects are anything but specific or characteristic.

A far truer and more productive definition would be based upon the study of the causes of a phenomenon, the unmasking of which should naturally throw much light upon the phenomenon itself and its probable effects.

The possible causes of allotropy may be either—(1) a variation in the intra-molecular structure of elements; or (2) a change in the inter-molecular association or aggregation of elements.

Considering that—

I. Molecular aggregation subject to the laws of crystallography accounts for polymorphism (Wyrubow, *Bull. Soc. Min.*, 1906, xxvii., 335), and that

II. Allotropic modifications present in most cases considerable chemical and physical differences—it would appear that allotropy is due to intramolecular differences (Koppel, *Naturw. Rund.*, 1904, xix., 249, 261; Guthrie, *Journ. Roy. Soc. N.S. Wales*, 1911, xiv., 318; Oxley, *Trans. Faraday Soc.*, 1916, xi., 129).

We can not only regard allotropy as a function of valency, but also define it as the capacity of an element to exist in forms, differing in the mode of their intra-molecular linkage.

This conception is in full accord with the (1) hypothesis of dynamic allotropy (Smits, *Proc. K. Akad. Wetens. Amsterdam*, 1910 and onward), as on this basis only a simple space lattice, revealed by the reflection of X-rays from the internal planes of crystals, can be deduced, and (2) the view of different ions existing in solution in presence of two allotropes of an element (Holt, *Journ. Soc. Chem. Ind.*, 1915, 693).

In this sense allotropy, although a function of valency, does not imply isomerism or polymerism, as all allotropes need not necessarily contain the same or a multiple number of atoms in their respective molecules.

The conception of allotropy as a function of valency can

be clearly understood on the basis of the electronic theory of the latter.

According to this theory the valency bonds are considered as having a definite direction. The relative direction of these bonds in the molecule may be influenced by the conditions under which such a molecule is formed. Variation in the direction would give rise to molecular structures differing in the distribution of the electric charges among the constituent atoms. These would be allotropes, and that configuration in which the charges were most symmetrically arranged or neutralised would be the stable form under these conditions (Holt, *loc. cit.*)

(This conception is closely related, if not identical, with the atomistic hypothesis according to which allotropy is due to changes in the electric and magnetic charges of an atom (Dumas, *Ann. Chim. Phys.*, 1831, [2], xlvii., 324; Howe, *Rep. Brit. Assoc.*, Sheffield, 1910 p. 562), as intra-molecular structures are primarily due to the properties and functions of the atoms).

Recognising allotropy as a function of valency and knowing the valency of an element (maximum in case of elements of variable valency), we should be able to indicate not only the possible constitutional formulæ of allotropes, but also the maximum possible number of allotropes for each individual element. (Without necessarily defining the number of atoms in the molecule, although the constitutional formulæ may in turn throw occasionally much light upon the complexity of the allotropes).

Attempting to represent elements by structural formulæ on the basis of their valencies, we find that monovalent elements can exist in one and only one molecular form (disregarding the ionic or nascent state), divalent elements may have two distinct allotropic forms. (Should elements exist in monoatomic molecules the number of modifications will be augmented by one):—

- (a) A molecular structure in which both valencies of the atoms are fixed, and
- (b) A molecular structure in which some valencies are free.

In the case of trivalent elements two allotropes are possible, being—

- (a) A saturated molecular configuration, in which all valencies are fixed, and
- (b) An unsaturated molecular configuration, in which some valencies are free.

In case of tetra-, penta-, and other polyvalent elements three allotropic forms are possible, being—

- (a) A rigid molecular form, in which all valencies are fixed;
- (b) A rigid molecular form, in which some valencies are free; and
- (c) A non-rigid molecular form, in which some valencies are free.

(On the basis of symmetry it is unlikely that a semi-rigid configuration, in which some atoms are rigidly fixed, whilst others retain the power of free rotation, should occur).

By molecular rigidity the author implies rigidity of atoms constituting the molecule, a rigidity caused by the fixation of the valencies. It appears that whilst an atom linked to two other atoms has the power of free rotation (the valencies being regarded as an axis), an atom linked to three or more atoms has no such power of rotation and can be regarded as rigidly fixed.

This gives the maximum number of distinct allotropes of an element under the most favourable conditions of temperature and pressure, forms possibly but not necessarily occurring in all physical states.

The examination of the chemical and physical properties of any element should enable us to determine the intra-molecular structure of each allotrope.

In trying to develop this hypothesis we must avoid a fallacy so general to many theories; i.e., being one-sided

in regarding various phenomena either as identical or totally disconnected with one another.

Continuity, harmonious continuity, is the most striking feature of natural phenomena when viewed as a whole.

The examination of separate most advanced members of any group, series, or species shows discontinuity, but continuity becomes manifest as soon as an effort is made to survey any phenomenon in all its gradations.

This certainly applies to such manifestations as physical states of matter, polymorphism and allotropy. The physical states of matter in their crystalline form, solid and liquid crystals, connect physical states with polymorphism. Polymorphism is, on the other hand, closely connected in many instances with allotropy.

A scrutiny of the possible molecular forms of elements shows that theoretically it is possible for an element to have in certain cases more than one molecular form corresponding to each mode of linkage indicated above; that is, there may occur more than one form of an element with a non-rigid or rigid configuration. But regarding allotropes as the most chemically and physically distinct forms of an element it is obvious that several molecular forms containing a different number of atoms, but all having the power of free rotation, will differ among themselves to a less extent than when compared with a molecular structure of the same element, in which all atoms are rigidly fixed.

Thus it follows that valency and the saturation or fixation of the atoms, and not the actual number of atoms, play the predominant part in the determination of allotropes. In this light allotropy becomes the capacity of an element to exist in forms differing in the mode of their intra-molecular linkage.

Molecular forms differing in the number of atoms or distribution of linkages, but all belonging to one and the same type of mode of linkage indicated above, can be termed *allotropoids*. These molecular forms serving as *tes* transition or link between polymorphism and allotropy proper can be compared with the cryptoisomeric substances (Pfeiffer, *Ber.*, 1916, xlix., 2426; 1918, li., 554).

Each modification of an element, which is an *allotropoid* in relation to forms belonging to the same mode of linkage is an allotrope, when viewed in connection with modifications belonging to a different type of linkage.

Allotropoids will differ among themselves less in physical and still less in chemical properties than *allotropes* of the same element.

The problem of discriminating between allotropy and polymorphism, or intra- and inter-molecular structures, comparatively easily solvable in the case of a few advanced characteristic instances, becomes therefore complicated and the available methods uncertain, not only owing to the inert character of some elements, which compels us to draw conclusions from their physical properties only, but also owing to the fact that in some cases we may deal with substances which are simultaneously either—(1) allotropes and polymorphic forms, or (2) *allotropoids* and polymorphic forms.

Thus the physical data may indicate the combined effect of intra- and inter-molecular rearrangements in the element, and as the components, the combination of which gives us the total effect, need not necessarily be magnitudes in the same direction, the physical data lose much even of their comparative value.

The knowledge of the maximum possible number of allotropes, serving as a guiding limitation, augmented by the chemical and physical properties of the modifications should be sufficient in most cases in identifying the allotropes of an element. In cases where owing to the inertness of an element we have to depend upon the physical factor only, as many physical properties as possible are to be taken into consideration, as no single feature or property is sufficiently characteristic as to serve as a decisive indication of allotropy.

The functional connection of physical constants with the periodic system of atomic weights and volume of elements make it very necessary, if any generalisations are to be

made, to have the experimental conditions for the determination of physical constants specific for every element with special relation to the absolute melting and transition points of every modification of an element.

Differences in crystalline symmetry are indefinite as a criterion or definition of allotropy owing to the possibility of substances belonging either to different crystalline systems or different classes of the same system. The observation that the higher the crystalline symmetry of an element the smaller is the number of atoms constituting its molecule (Relgers, *Zeit. Phys. Chem.*, 1894, xiv., 1), and consequently the smaller is its tendency to allotropy (Barlow and Pope, *Journ. Chem. Soc.*, 1906, lxxxix., 1741) is of an empirical character, and can hardly serve as a guiding principle in distinguishing between allotropic from polymorphic forms, this being specially so as crystalline structures may depend at least as much upon molecular aggregation as on the intra-molecular configuration of the atoms.

The sudden changes in and the discontinuity of properties can be accepted as an indication of allotropy, but with reserve, not only owing to the difficulty of establishing such discontinuity (Honda, *Journ. Iron and Steel Inst.*, 1915; *Science Rep.*, Tokio, 1915, [IV.], No. 3, 261), but also owing to the fact that such changes accompany both allotropy and polymorphism, and if there is any difference it is in the degree not the kind of change.

The thermal changes so characteristic of the most pronounced allotropic transformations of the non-metallic elements, though often very useful as an indication, are not completely to be relied upon, as all thermal measurements for metals give decidedly lower values than for non-metals, and considerable changes of volume, hardness, porosity, electromotive forces, electrical resistance, specific heat, and thermoelectric power are not necessarily accompanied by great heat changes.

Considerable heat changes may be taken as a positive indication of allotropic rearrangement, but small heat changes are hardly safe as a negative proof, the more so as the heat evolution actually recorded may be the sum of two or more values or reactions, some exothermic and others endothermic.

As mentioned above, the allotropes of metals are more difficult to isolate and distinguish than those of the non-metals owing to their inert character. But even in cases where no separate allotropic modifications were isolated, (1) the dependence of such physical properties as density, specific heat, expansion, electrical conductivity, and the melting, solidification, and transition points upon the thermal history of the specimen, and (2) the variation of the chemical behaviour with the past history of the metal—are best explained on the basis of the allotropy hypothesis.

The occlusion of hydrogen by palladium and palladium black, the etching of iron by nitric acid, and the solubility of carbon in α and γ iron can be quoted as such extreme cases.

The constitutional formulæ of allotropes developed on the basis of valency and the chemical and physical properties of each modification, although not actually solving the interesting problem of molecular complexity, offer us substantial aid in this respect, in so far as they often indicate the minimum molecular complexity satisfying the requirements of the formulæ.

HIS MAJESTY THE KING, on the recommendation of the President of the Board of Trade, has been pleased to award the Silver Medal for Gallantry in Saving Life at Sea to each member of the crew of the Danish s.s. *Mary*, which rescued Mr. Harry George Hawker and Commander Kenneth F. Mackenzie-Grieve, R.N., in the North Atlantic on May 19. The Board of Trade, with approval of His Majesty, have also awarded pieces of plate to the master of the ship and to the person in charge of the rescuing boat, and sums of money to the rest of the boat's crew.

A PRECISION PRESSURE GAUGE.*

By EDWARD J. BRADY.

THIS note is a brief description of a precision pressure gauge of high sensibility and great accuracy recently constructed at this Laboratory.

In principle it is virtually a large diameter U-tube (6 cm. diam.) filled with some transparent non-volatile, non-oxidising liquid such as kerosene or paraffin oil. In each leg is placed a hollow brass float. The two floats are connected together with a fine silk thread which passes downwards around a light graduated wheel with jewel bearings immersed in oil at the bottom. The position of the wheel, which is provided with a vernier, is read through a glass window in one end of the box that forms the bottom of the gauge.

Laboratory workers having to do with the accurate measurement of small gas pressure, either plus or minus, are greatly in need of an instrument similar to the one to be described.

The way in which the differential pressure enters in the formulæ for both the Venturi meter and the Pitot tube may be represented by $P = (f) Q^2$, where P is the pressure that must be read and Q is the quantity of material passed. It will be seen that both of the methods become increasingly inaccurate at low velocity, because of the difficulty of measuring small pressures accurately. This gauge ought to increase the usefulness of both the Venturi and the Pitot tube.

A modification of the gauge with an opening to receive the horizontal velocity pressure of the wind might be used as an anemometer.

The two glass cylinders are cemented into the removable cover of a brass box, one end of which has a glass window. To the lower side of the cover is fastened the little yoke supporting the two jewel bearings in which the index wheel or drum revolves. To one arm of this yoke is fastened a projecting piece carrying a vernier flush with graduate surface of the wheel. There is a small groove on the face of the wheel around which passes the silk thread that holds the two hollow floats almost totally immersed in the fluid. Any pressure P on this liquid in one tube produces a linear motion at the circumference of the

wheel of $\frac{P}{2}$

The diameter of the wheel was so chosen that a pressure of one inch of distilled water exerted on a paraffin oil, such as kerosene, produces a motion of the periphery of the wheel of 10 divisions. By the aid of the vernier this precision can be increased.

These cylinders are made of glass, so that the gauge can be read approximately and from a distance like an ordinary U-gauge with the inch mark on the scale between the two cylinders.

Its use as a zero reading instrument capable of indicating pressure differences of less than 10^{-3} inches of water, will now be described.

Upon the little shaft that carries the graduated wheel there is fastened a small mirror, arranged to face toward the glass window in the lower position. About 4 feet in front of the gauge there is mounted a telescope and scale. This can only be used for comparatively small variations in pressure, say less than $2/10''$. However, the telescope and scale may be used to measure small differences at pressures of, say, $2''-3''$ and $4''$, by moving the mirror around on the shaft, so that it has the proper aspect when the gauge is subjected to the above pressures.

This is facilitated by a small bent movable wire, projecting through a stuffing box in the side. It is pushed in sufficiently to interfere with the rotation of the mirror until the float assumes the position corresponding with

the pressure whose small variation is to be measured. It is then withdrawn, when the telescope and scale can be used as before.

The glass window may be made a section of a cylinder, so that all rays from the scale would pass normally through the glass, eliminating refraction effects, but this was not found necessary in practice.

The instrument as constructed has twin hollow brass floats and a brass wheel below. The bearings are jewelled, with very little friction. The friction may easily be made as near zero as is possible by making the wheel of aluminium and so proportioning it that the weight of the wheel in the oil used is just equal to the buoyancy of the two floats.

Even with the brass wheel having some weight on the bearings, the system has a very definite zero. The motion of the mirror for small displacements is almost critically damped.

The instrument may be dismantled by inserting two small wire hooks through the hose connections at the top to support the floats while the oil flows out at the bottom.

A gauge constructed as above described has been in use at this laboratory and has given entire satisfaction. When not in use a small piece of rubber tubing is connected from one inlet to the other to keep the dust out. With an ordinary U-gauge an accumulation of dirt invariably appears at the point where the menisci are read; with this gauge, however, the graduations on both the wheel and the vernier are immersed in the oil and always appear bright and clean.—*Journal of the Franklin Institute*, clxxxvii., No. 4.

THE ELECTROLYSIS OF SOLUTIONS OF THE RARE EARTHS.*

By L. M. DENNIS and B. J. LEMON.

Historical.

BUT little attention appears to have been paid to the possibility of separating the rare earths by electrolysis of aqueous solutions of their salts. Edgar F. Smith (*Ber.*, 1880, xiii., 751) stated that "didymium is not precipitated, either as nitrate or acetate, although a partial precipitation takes place at the positive pole." Brauner (*Monatsh.*, 1882, iii., 1) electrolysed a solution of didymium acetate using platinum electrodes. There formed on the negative pole a pale red crystalline crust which contained didymium and acetic acid. Solutions of the nitrate and of the sulphate of didymium gave similar products. Brauner's object in these experiments was to ascertain whether a superoxide would appear on the positive pole. No such formation was noted, and he did not pursue the subject further. In a brief article entitled "Electrolysis of Solutions of the Rare Earths" (*Zeit. Anorg. Chem.*, 1893, iii., 60) Krüss makes the following statement:—"A solution of a chloride of a rare earth behaves upon electrolysis like a solution of an hydroxide in dilute hydrochloric acid; chlorine and hydrogen are set free at the electrodes, the solution loses more and more hydrochloric acid, and as the amount of the solvent diminishes, the hydroxide of the earth is precipitated in increasing amount. In this manner the rare earths can be removed from chloride solutions of mixtures of the earths, the amount thus precipitated depending upon the strength of the current and the duration of the electrolysis. It is to be expected that those bases which are the weakest toward hydrochloric acid will first be precipitated as hydroxides as soon as a part of the hydrochloric acid is decomposed by the electrolysis. The stronger bases will remain in solution as the more stable chlorides. In order to remove the hydrochloric acid uniformly from all parts of the solution

* Note from the Physical Laboratory of the United Gas Improvement Company, U.S.A.

* From the *Journal of the American Chemical Society*, xxxvii. No. 1.

of the chlorides of the rare earths, electrodes of large surface were employed." Krüss electrolysed the solution for ten minutes, and then removed the heavy, dense deposit of hydroxide by filtration. The solution was then again electrolysed for ten minutes, and in this manner small fractions of less than 1 gm. each were obtained. Two electrolyses of solutions of impure yttria were carried out, and determinations of the atomic weights of the

cerium salts with platinum electrodes, but inasmuch as this does not concern the direct separation of the earth from solution upon electrolysis, the researches upon this subject will not here be reviewed.

Experimental.

Material.—The material that was employed in the experiments described below consisted of the earths of

Original
solution.

Fract. 5.

Fract. 8.

Residual
solution.

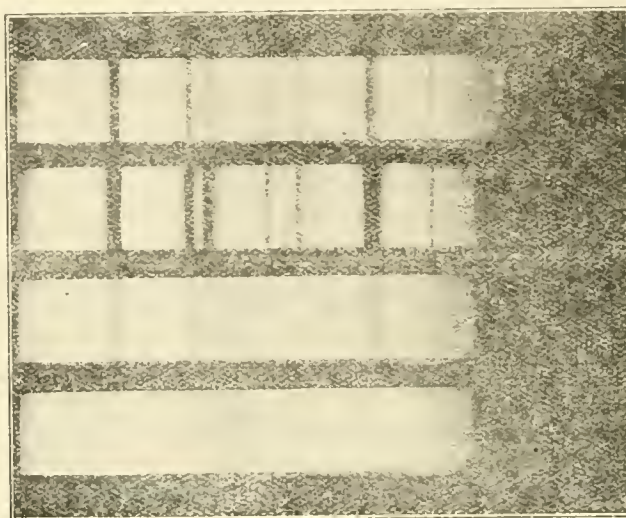


FIG. 1.

Original
solution.

Fract. 4.

Fract. 5.

Fract. 6.

Residual
solution

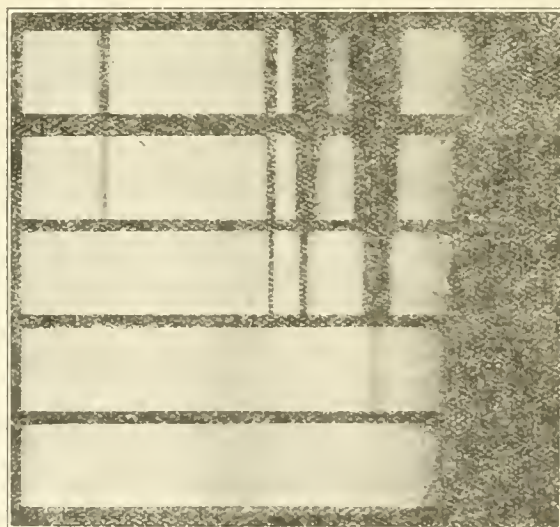


FIG. 2.

earths in the several fractions showed that the method gave quite rapid separation of the different earths. Krüss states at the close of this brief article that electrolysis of solutions of the rare earths might prove suitable for the separation of these elements. It does not appear, however, that he followed the matter further.

Considerable work has been done upon the anodic oxidation of cerium through electrolysis of solutions of

both the didymium and yttrium groups from which cerium and thorium had been removed. The earths of the didymium group were extracted from the crude double sulphates of potassium and the didymium group, a large amount of this material having kindly been presented to the writers by Dr. H. S. Miner, of the Welsbach Light Company. The lanthanum and praseodymium nitrates were prepared from quite pure samples of these two salts

that we owe also to the kindness of Dr. Miner. The earths of the yttrium group were obtained from the crude rare earth oxalates from xenotime; the mixture that was used in the experiments showed strong absorption bands of erbium, and rather faint bands of europium, samarium, and holmium. The didymium bands were very faint.

Apparatus.—The first electrolysis was performed in a small crystallising dish and stationary electrodes of sheet platinum were used. On electrolysing a slightly acid solution of the nitrates of the didymium group, no precipitation appeared until the free nitric acid had been broken down by the current. As soon as this had been effected, however, a separation of the hydroxides of the earths appeared at the cathode, and the internal resistance of the cell rapidly increased. Upon interrupting the current and examining the contents of the cell it was found that a portion of the hydroxides had separated in flocculent form resembling aluminium hydroxide, and also that that part of the cathode which was immersed in the solution was heavily covered with a dense granular precipitate of the hydroxides. It was this coating of the

surface of this mercury cathode was kept clean by violently agitating it by jets of air, the air being conducted into the mercury through a glass tube with three outlets. The anode consisted of a piece of platinum wire 0.76 mm. in diameter. The source of current was a set of eight storage cells, an ammeter and variable resistance were placed in series with the cells and a voltmeter was connected in shunt with the cell. The aqueous solution of the rare earths that was to be subjected to electrolysis was placed in the cell upon the surface of the mercury.

1. Separation of Lanthanum from the Other Earths of the Didymium Group.

A neutral solution of the nitrates of the rare earths neodymium, praseodymium, lanthanum, and samarium, that contained 50 grms. of the oxides of the earth in one litre of the solution, was placed upon the mercury cathode in the cell, the mercury was set in agitation by a blast of air, the current was turned on, and the voltage was gradually stepped up to a point where fairly rapid precipitation of the hydroxides took place. The voltage was

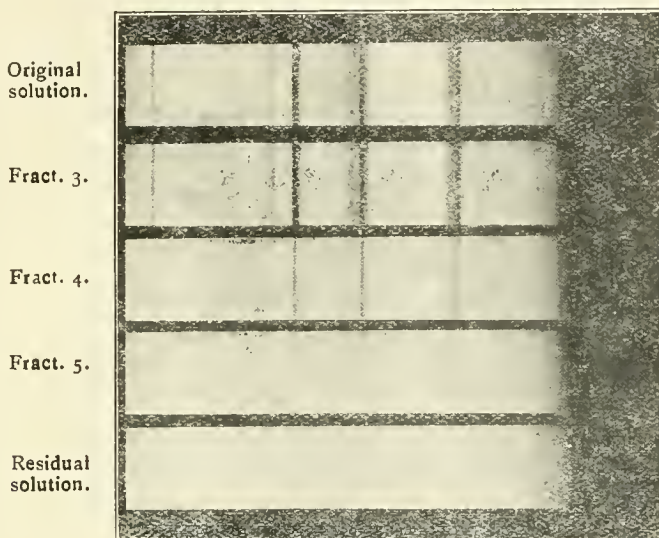


FIG. 3.

cathode surface that interfered with the passage of the current and caused marked fluctuations in the voltage.

It was thus evident that no definite voltage could be maintained for any considerable length of time unless the cathode surface could be kept free from deposit of the hydroxides. To attain this end, a rotating cathode of copper in the form of a wheel 15 cm. in diameter and 2.5 cm. in thickness was next employed. This was mounted on a horizontal shaft of the same material and was set in such a position that the wheel dipped into the solution of the nitrates of the earth to a depth of three centimetres. An anode of platinum was used. A copper scraper was fastened in such position that it rested against the edge of the cathode wheel, and it was hoped that by means of this arrangement the deposit of hydroxides upon the cathode might rapidly be removed, and the voltage in this manner be kept sufficiently constant to permit of fractional decomposition of the different nitrates in solution. The apparatus did not give satisfactory results, and after thorough trial it was abandoned, and a mercury cathode was employed. The mercury was placed in a glass cell about 12 cm. in diameter and 13 cm. high, the layer of mercury being about three centimetres deep. The

maintained constant at this value, 9 volts, throughout the series of fractionations, and this voltage was used in the three fractional electrolyses described below. The first fractional electrolysis was of six hours' duration. The current was then turned off, the hydroxides were allowed to settle, the clear supernatant liquid was siphoned off, and the remaining solution was separated from the precipitate by filtration through a Büchner funnel. The filtration was then returned to the cell and was again electrolysed. In this manner eleven fractions were obtained. The hydroxides of each fraction were first thoroughly washed with hot water, were then dissolved in hydrochloric acid, and the small amount of mercury that they were found to contain was removed by double treatment with hydrogen sulphide. The rare earths in the solution were then precipitated from a slightly acid solution with oxalic acid, were thoroughly washed, and were then ignited to the oxides. The atomic weights of the rare earth elements were determined by igniting one portion of the oxalate to oxide and determining the oxalic acid in another portion by titration with potassium permanganate. The details of this run are shown in Table I.

TABLE I.

Number of fractions.	Time in hours.	Colour of oxides.	Atomic weights (original material, 140.6).
1.	6	Light brown	140.9
2.	5	Light brown	141.2
3.	7	Light brown	141.5
4.	6	Light brown	141.9
5.	4	Colour fading	141.7
6.	5	Colour fading	141.0
7.	4	Colour fading	140.4
8.	5	Colour faint	139.6
9.	3	Colour very faint	139.5
10.	4	White	139.0
Residual solution		White	138.9

The absorption spectra of the original solution of Fractions 5 and 8 and of the residual solution were photographed with the aid of a Hilger wave-length spectrometer, Model 1912, with an oxyhydrogen zirconia lamp as the source of illumination. The different solutions used were of the same concentration in respect to the weight of the rare earth oxides contained in a unit volume. For photographs in black and white the Cramer trichromatic plate, which is especially sensitive to the red, was found to give quite satisfactory results. (Fig. 1).

II. Separation of Lanthanum from Praseodymium.

Nineteen and six-tenths grms. of fairly pure praseodymium dioxide and 18.9 grms. of lanthanum oxide were mixed, dissolved in nitric acid, the solution twice evaporated to dryness, redissolved in water, and diluted to 500 cc. Upon electrolysis of this solution the results showed in Table II. were obtained.

The atomic weights of the rare earth elements in these fractions were determined by the method mentioned under I. Inasmuch as praseodymium was present, the active oxygen in the ignited oxide was determined by the Bunsen method, and this was deduced from the weight of the oxide in order to arrive at the amount of Pr_2O_3 that was present. That the atomic weights of the earths in Fractions 1 to 4 inclusive were higher than that of praseodymium is due to the fact that small amounts of other earths of this group were present.

TABLE II.

Number of fractions.	Time in hours.	Colour of oxides.	Atomic weights (original material, 141.2).
1.	9	Black	142.1
2.	7	Black	141.9
3.	8	Dark brown	142.0
4.	9	Brown colour fading	141.7
5.	8	Brown colour faint	140.3
6.	7	Brown colour very faint	139.5
Residual solution		White	138.8

Photographs of the original solution, of Fractions 4, 5, and 6, and of the residual solution are produced in Fig. 2. It will be noted that lanthanum is freed from praseodymium by a very small number of fractional electrolyses.

III. Fractional Electrolysis of the Earths from Xenotime. Separation of Erbium from Yttrium.

Six fractional electrolyses were made with the results as set forth in Table III.

TABLE III.

Number of fractions.	Time in hours.	Colour of oxides.	Atomic weights (original material, 103.83).
1.	10	Light yellow	104.89
2.	8	Light yellow	111.00
3.	9	Light yellow	109.23
4.	7	Light yellow	99.73
5.	8	Faint yellow	93.50
Residual solution		Very faint yellow	92.08

Photographs of the original solution, of Fractions 3, 4, and 5, and of the residual solution are reproduced in

Fig. 3. It will be noted that erbium concentrated chiefly in the first three fractions and that in the succeeding fractions its amount rapidly decreased. The atomic weight of the rare earths in the final fraction, No. 6, was 92, which demonstrates the rapidity of the concentration of yttrium by this method.

The results of the experiments here described upon the fractional electrolysis of different mixtures of the rare earths appear to warrant the statement that the method yields quite rapid separations of some of the rare earths, and that these separations can be effected with far less expenditure of time and labour than by the customary methods of fractional crystallisation or fractional precipitation.

MECHANICAL PHILOSOPHY AND SURFACE TENSION.

By FRED G. EDWARDS.

WHEN an ether atom of mass 0.8×10^{-24} gm. impinges upon a chemical atom of much larger mass the velocity of the ether atom is reduced in the proportion $f/(M+m)$. Above the critical temperature and below the critical pressure of a gas, this would be compensated in the inverse ratio by the impact of a chemical atom upon an ether atom, so that the ether atoms in the interspaces of the gas would have the same average velocity as in the free ether. But, immediately the temperature is reduced and the pressure increased, the chemical atoms impinge upon each other to form the infinite molecule of the liquid or solid condition and the compensation of the ether atom is lost. This period corresponds with the formation of the meniscus in the vacuum tube or the tension surface surrounding the liquid. The reduction of ethereal atomic velocity produces a reduction of intrinsic pressure in the proportion $f_1[M/(M+m)]^2$, or a fraction of the ethereal pressure 0.5×10^{24} dynes, of higher order than that of the critical or atmospheric pressure $N \times 10^6$ dynes. The magnitude of the term $a/v^2 = 11,000$ atmospheres obtained from Van der Waals's equation $(p + a/v^2)(v - b) = RT$, which is the estimated intrinsic molecular pressure of water, need no longer be surprising, as the intrinsic ethereal pressure is infinitely greater. Laplace's equation $P = K \pm H/R$ now admits of two opposing physical interpretations each a function of the mass and concentration of the molecules, one being direct action at a distance with an assumed radius of molecular attraction, and the other the measurable action of an incompressible fluid. In the latter case the intrinsic pressure is seen to be in reciprocal ratio to the compressibility, which is the elasticity of the material. It has been tacitly assumed that the free ether, and likewise the bound ether, are incompressible fluids; that is to say, the ethereal atomic volume is constant by reason of interaction through the tension surfaces.

The neutralisation of one monobasic acid molecule or of one ion of a polybasic acid at standard temperature yields 13,700 (6.1×10^{23}) calories with one electron. The heat of reaction is independent of the nature of the anion and cation, and equal to the quantity of heat required for the dissociation of water, which of course varies inversely with the temperature and therefore directly with the surface tension. The work required to force an electron into a metal or out of a liquid is thus a function of the surface tension, and likewise contact potential will be a function of the two surface tensions.

The difference in thermal energy of an electron inside a liquid and that of a free electron may be measured by the relative energies of its positive ether atom. The energy of the positive atom of free ether = 1.058 erg. can be calculated from two different data stated in grms. and centimetres:—

$$U = \frac{2}{3} p v = \frac{2}{3} (5175 \times 10^{17}) (1.39 \times 10^{-24}) \quad (1).$$

$$U = \frac{2}{3} m C^2 = 0.4 C^2 \times 10^{-24} \quad (2).$$

Incidentally from (1) and (2) the velocity of the ether atom is obtained. $C = 5.193 \times 10^{10}$, or $3\sqrt{3} \times 10^{10}$ cms./secs. This is $\sqrt{3}$ times the radiation velocity and $\sqrt{3}$ is $\tan 60^\circ$, proving that the path of the ethereal atom coincides with four edges of a regular tetrahedron, thus completing the theory of an atomic ether described in a former paper (CHEMICAL NEWS, 1919, xcvi., 183), and showing that the atom does not reciprocate in a rectilinear path which would be the hypothetical alternative motion in a dodecabedral formation with double plena.

In the liquid the reduction of energy:—

$$\Delta U = 13,700 \times 4.188 \times 10^7 / (6.1 \times 10^{23}) = 9.405 \times 10^{-15} \text{ ergs (3).}$$

$$v = \text{constant} = 1.39 \times 10^{-24} \text{ cc.}$$

$$\Delta p = \frac{2}{3} \Delta U / v = (6270.3 \times 10^{-15}) / (1.39 \times 10^{-24})$$

$$= 4.51119 \times 10^{11} \text{ dynes/cms.}^2 \quad \dots \dots (4).$$

In a dilute solution this would be the intrinsic molecular pressure of water. Hitherto it has been deemed impossible to directly determine this pressure, and the accepted estimates of 1.1×10^{10} dynes require to be multiplied by 41.

If the intrinsic pressures, as now suggested, are exactly determined by the heat of neutralisation, the value of the unknown term dp/dT in the Clausius equation $dp/dT = -L/[T(v_2 - v_1)]$ can be calculated. Moreover, if the Eötvös formula be true, namely, $\sigma/M\rho^{\frac{2}{3}} = K(\theta - 6)$, the surface tension of a single molecule is obtainable with the weight of the molecule or molecular aggregate, and as the periodic specific volumes and the periodic specific entropies of the elements are measurable they can all be shown to be functions of the atomic shapes, which recur in accordance with the periodic table when the chemical atoms are built up symmetrically with the ether atom as the tetrahedral unit.

GALLIUM.*

By L. M. DENNIS and J. ALLINGTON BRIDGMAN.

(Continued from p. 258).

THE DETERMINATION OF GALLIUM ALONE, AND OF GALLIUM, INDIUM, ZINC, AND ALUMINIUM IN THE PRESENCE OF ONE ANOTHER.

The Determination of Gallium.

LECOQ DE BOISBAUDRAN determined gallium by adding to a solution of a salt of gallium an excess of ammonium hydroxide and then boiling the solution until it turned litmus-paper red. (*Ann. Chem. Phys.*, 1884, [6], ii., 181). This precipitated the gallium as the hydroxide, and Boisbaudran stated that the presence of salts of the alkali metals or of the alkaline earths did not affect the results. From 1 to 1.5 mgrm. of gallium per litre of solution was, however, unprecipitated.

Trial was made of this method of Boisbaudran by adding ammonium hydroxide to a solution of gallium chloride that contained about 0.05 gm. of gallium oxide. The solution was then boiled, and it was found necessary to continue the boiling for from thirty to forty-five minutes to effect the removal of the excess of ammonium hydroxide. Although the precipitate of gallium hydroxide was somewhat granular much of it adhered to the sides of the beaker and could not be detached. Another portion of the solution of gallium chloride was precipitated by ammonium hydroxide after ammonium chloride had first been added. The precipitate in this case was somewhat more gelatinous, but a portion of it adhered firmly to the sides of the beaker.

* This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by J. Allington Bridgman in partial fulfilment of the requirements for the degree of Doctor of Philosophy. From the *Journal of the American Chemical Society*, xl., No. 10.

Because of this difficulty two other precipitants were next tried, and to render it possible to ascertain the accuracy of these new methods a solution of gallium of known concentration was prepared from some of the gallium chloride that had been purified by distillation. A sample of this gallium chloride was dissolved in water, an excess of ammonium hydroxide was added, and the resulting gallium hydroxide was washed, dried, and ignited to gallium oxide over a Bunsen flame. This oxide was then pulverised in an agate mortar, was reheated, and was then cooled in a stoppered weighing bottle. 0.6471 gm. of this oxide was heated with 1.5 cc. of concentrated sulphuric acid, the resulting gallium sulphate was dissolved in water, and the solution was diluted to 250 cc. in a measuring flask. This flask was calibrated to hold ten times the volume of a 25 cc. burette that was subsequently used to measure portions of the solution.

The first reagent that was used for the precipitation of the gallium was sodium trinitride, NaN_3 .

Precipitation of Gallium Hydroxide by Sodium Trinitride.—Portions of 25 cc. each of the slightly acid solution of gallium sulphate just described were diluted to about 250 cc. Solid sodium trinitride was added to each solution, and the solutions were then vigorously boiled for various lengths of time. The resulting precipitates of gallium hydroxide, which settled well, were collected on ashless filters, and were washed, dried, and ignited to gallium oxide over a Bunsen flame. The oxide was in each case ignited in a porcelain crucible, was cooled in a desiccator, and was then quickly weighed.

In determination No. 3, in which the boiling was continued for ten minutes, the precipitate adhered somewhat to the sides of the beaker, and this explains the low weight of gallium oxide. When the solution was boiled for a shorter time, Nos. 1, 2, and 4, the results were fairly satisfactory in each case, and the presence of as much as 15 grms. of ammonium chloride did not affect the accuracy of the method. The use of sodium trinitride, however, is open to two objections: the powerful physiological action of the hydronitric acid that is liberated when the solution is boiled, and the difficulty of obtaining on the market a supply of sodium trinitride of satisfactory purity. For these reasons sodium sulphite was substituted for sodium trinitride.

TABLE V.—Precipitation of Gallium Hydroxide by Sodium Trinitride.

	1.	2.	3.	4.
Weight of Ga_2O_3 taken (grm.) ..	0.0647	0.0647	0.0647	0.0647
Weight of NaN_3 added (grm.) ..	0.5	0.5	0.5	0.5
Time of boiling (minutes) ..	1—2	5	10	4
Other salts added..	None	None	None	5 g. NH_4Cl
Weight of Ga_2O_3 found (grm.) ..	0.0630	0.0660	0.0623	0.0657

Precipitation of Gallium Hydroxide by Sodium Sulphite.

—A portion of the same solution as was used above was precipitated by adding about 1 gm. of solid hydrated sodium sulphite to the solution and boiling for four minutes. The precipitate was easily collected by filtration, but ignition to the oxide showed that precipitation had not been complete. 0.0784 gm. of gallium oxide was present in the solution, and the precipitate weighed 0.0728 gm. A further small amount of sodium sulphite was added to the filtrate, which was again boiled, and the precipitate yielded on ignition 0.0054 gm. of gallium oxide. In the precipitation of further portions of the solutions 1.5 grms. of sodium sulphite was added in each case. The results are given in Table VI.

The results are quite satisfactory even when fairly large amounts of ammonium salts are present. It was found that the solutions could be boiled for a much longer time

than when sodium trinitride was used, without causing the precipitate to adhere to the walls of the beaker.

TABLE VI.—*Precipitation of Gallium Hydroxide by Sodium Sulphite.*

	1.	2.	3.
Weight of Ga_2O_3 taken (grm.)	0.0647	0.0647	0.0647
Time of boiling (mins.)	10—12	6—7	7
Other salts present (to grms.)	NH_4Cl	NH_4NO_3	$(\text{NH}_4)_2\text{SO}_4$
Weight of Ga_2O_3 found (grm.)	0.0649	0.0661	0.0641

A slight modification of this method of precipitation, which avoids the introduction of sodium salts into the solution, was later employed in the determination of gallium in a sample of caesium gallium selenate alum (see *prox.*). A solution of ammonium sulphite, which was prepared by saturating ammonium hydroxide with sulphur dioxide, was substituted for solid sodium sulphite. A value of 13.33 per cent of Ga_2O_3 as against a calculated value of 13.31 per cent in the alum was obtained.

In making weighings of gallium oxide it was observed that this substance, like the oxides of aluminium and indium, is quite hygroscopic, and in all of the analyses that are later described the crucible that contained the gallium oxide was placed in a stoppered weighing bottle as soon as it was removed from the desiccator, and was weighed in that bottle.

In the determinations of gallium described below gallium was precipitated by sodium sulphite, the procedure being as follows:—If ammonium chloride or hydrochloric acid is not already present in the solution, a few cc. of hydrochloric acid is added, the solution is then made slightly alkaline with ammonium hydroxide, and about 1.5 grms. of hydrated sodium sulphite is dissolved in the solution. This weight of sodium sulphite suffices for the precipitation of 0.1 gm. of gallium oxide, and the amount of gallium should usually not be permitted to exceed this amount because otherwise the precipitate of gallium oxide is so bulky as to render difficult its filtration and washing. After the sodium sulphite has been dissolved in the solution hydrochloric acid is carefully added until the solution is distinctly acid to litmus-paper. The solution is then vigorously boiled for about six minutes. The resulting precipitate of gallium hydroxide is allowed to settle, and is then filtered on an ashless filter-paper and washed until the wash water is free from chlorides. The precipitate is dried and is ignited with the paper over the Bunsen flame in a porcelain crucible. The crucible is placed in a desiccator while still warm, and is afterwards transferred to a stoppered weighing bottle for weighing.

The precipitation of gallium by this method is usually complete, but it nevertheless is advisable to add a small amount of sodium sulphite to the filtrate, and to boil that for some minutes to ascertain whether gallium is present. If insufficient hydrochloric acid was added before the solution was first boiled some gallium may be retained in solution by the alkali resulting from the hydrolysis of the sodium sulphite. To guard against this error the filtrate, after boiling with a small amount of sodium sulphite and the removal of any precipitate that may form, should be acidified with acetic acid and boiled for twenty minutes. Any gallium hydroxide that appears on this treatment is collected, ignited, and weighed, and its weight added to that of the oxide already obtained.

Precipitation of Zinc as Zinc Mercuric Thiocyanate from Solutions that contain Gallium.

Zinc forms a difficultly soluble double salt with mercuric thiocyanate. Gallium does not. To ascertain whether this fact could be utilised to separate zinc from gallium, a solution that contained the sulphates of gallium and zinc

was made slightly acid with sulphuric acid, and an excess of a solution of potassium mercuric thiocyanate was added. After several hours the precipitate of zinc mercuric thiocyanate was removed by filtration. The filtrate was treated with hydrogen sulphide to precipitate the mercury, the mercuric sulphide was filtered off, the filtrate was boiled to remove hydrogen sulphide, and ammonium hydroxide was then added until the solution was slightly alkaline. Acetic acid was next added in slight excess, and the gallium that was present was precipitated as the hydroxide by boiling this solution. This hydroxide was dissolved in a slight excess of sulphuric acid, the solution was diluted to 100 cc., and the metals in the resulting solution were fractionally deposited by electrolysis on a rotating platinum rod, using a current of 2 to 3 amperes. Spectroscopic examination of the deposits on the cathode showed that zinc and gallium were present in all of them, zinc predominating in the early fractions and gallium in the later ones. These results showed that zinc was not completely precipitated by potassium mercuric thiocyanate under the conditions above described.

While this work was in progress, however, an investigation of this method for the determination of zinc was completed in this laboratory by Mr. C. S. Hoyt (see Note) working under the direction of Prof. G. E. F. Lundell. These investigators established the conditions under which the precipitation of the zinc should be made, and careful observance of their directions gave us very satisfactory results.

(NOTE.—“The Zinc Mercuric Sulphocyanate Method for the Determination of Zinc,” a thesis presented to the Faculty of the Graduate School of Cornell University, June, 1917; also Lundell and Bee, *Trans. Am. Inst. Metals*, Sept., 1914).

The reagent is prepared by dissolving 27 grms. of mercuric chloride and 39 grms. of potassium thiocyanate in 1 litre of water. The solution of the zinc salt to be precipitated should not contain more than 0.1 gm. of zinc in 200 cc., and this volume of solution should contain about 2 cc. of concentrated nitric acid or sulphuric acid. The solution of potassium mercuric thiocyanate is added by drops to the solution of zinc, which is constantly stirred during the addition of the precipitant. In making a determination of zinc the reagent is added until a precipitate begins to form, and from this point 20 cc. of the precipitant is added for every 0.1 gm. of zinc estimated to be present. After precipitation is complete the contents of the beaker are allowed to stand for several hours. The precipitate is then collected in a Gooch crucible, is washed with water that contains 20 cc. of the reagent per litre, and is then dried at 105–110°. The zinc factor for this precipitate is 0.1314.

The accuracy of the separation of zinc from gallium by this improved method was tested by precipitating the zinc from a slightly acid solution containing known amounts of zinc and gallium. After the precipitate of zinc mercuric thiocyanate had been removed by filtration 10 cc. of hydrochloric acid was added to the filtrate and the mercury in the solution was precipitated by hydrogen sulphide. The mercuric sulphide was filtered off, the filtrate was boiled to expel hydrogen sulphide, and the gallium was then thrown down by sodium sulphite (see above), and was weighed as the oxide. The results of two analyses, which are given in Table VII., show that the method is quite satisfactory for the determination of zinc and gallium in the presence of each other.

TABLE VII.—*The Separation of Zinc from Gallium.*

	1.	2.
Weight of zinc taken (grm.)	0.0939	0.0939
Weight of zinc found (grm.)	0.0929	0.0937
Weight of gallium oxide taken (grm.)	0.0828	0.0828
Weight of gallium oxide found (grm.)	0.0823	0.0830

[To be continued.]

INDUSTRY AND HIGHER EDUCATION.

A MEETING was held on Tuesday, May 20, between representatives of the Universities and Colleges and representatives of the Federation of British Industries.

Sir RICHARD VASSAR-SMITH, Bart., presided over the gathering, and in his introductory remarks stated that the meeting had been called to consider the setting up of an organisation which might act as a clearing house between Universities and the Industries of the country.

It was desired to make some arrangements by which young men leaving the Universities would have the opportunities of passing into productive work, which would give full scope to their abilities and education. Such an organisation should enable the man of real merit to obtain a post which would allow him to use his abilities to the fullest extent.

Personally he felt there was need of such an organisation, as in the future it would be more imperative than ever that each man, in whatever grade, should be working efficiently. There was a need in industry for a supply (and the maintenance of that supply) of the best intelligence of the country. It was in order to discuss this question that the meeting had been called.

Mr. H. A. Roberts, of Cambridge University, stated that the suggestion was one which would meet with approval by all interested in national wellbeing. There were difficulties in setting up such an organisation, and it might be advisable in the first case to limit the activities until further experience had been gained. It was very undesirable to innovate a scheme on too grand a scale until experience had been obtained.

Prof. Ferrier, of Bristol University, pointed out that there had been no difficulties in placing the really first-class men, but men of the second class certainly needed assistance. In many cases the second-class men had made good when they had been able to obtain a position which offered scope; ability was not confined to academic distinction; especially was this the case in regard to work in Industry and Commerce. As a rough estimate he would say that 5 per cent of the first-class University men would be required for research purposes. The remaining 95 per cent would be employed as ordinary routine business men. There had been a marked tendency for the University trained men to proceed overseas, and even in the United States the English University man was generally sure of finding employment. It was to be hoped that this exodus of the finer grade of worker would be stopped by the offer of suitable employment in this country.

Prof. Baker, of the Imperial College of Science and Art, stated that he was in full agreement with the last speaker, and that the real difficulty was in fixing the second grade student, although there must really be a demand for them. In the chemical industry, for instance, there was routine work which would be more ably carried out by the trained man. In most cases, at present, this was carried out by the ordinary worker. The value of the well trained man in routine work was not appreciated at present, and he hoped that by the scheme which had been outlined the Employer would eventually come to the Organisation for such men besides the super-men of research.

Prof. Lea, of Birmingham University, hoped that the scheme would include all grades of men. Industry needed all grades, and education could never hope to produce men of one grade only. He thought the Federation, being such a thoroughly representative body, could best tackle this scheme, which he felt would encourage closer co-operation between the University and Industry.

The Master of Pembroke College, Cambridge, stated that there had been a great increase in the number of employers who were now sending their sons for University training; this was an excellent sign, and should help eventually in obtaining the co-operation for which Prof. Lea hoped.

Prof. Bulleid, Nottingham University, hoped that the

institution of such an organisation would not mean putting another barrier between the student and the possible employer; he had always found that the most satisfactory method for obtaining posts was for the student to write to the employer direct.

Dr. R. A. Duff, of Glasgow University, suggested that it might be found that centralising vacancies in the proposed Clearing House might be the best way of tackling the problem. This was a question of administration and would no doubt be considered before fully settling the scheme.

Miss M. H. Mead, of Manchester University, asked whether the organisation would deal with women. In reply it was stated that the term "students" had been expressly used in the Memorandum as meaning to convey that both men and women were included in the scheme.

It was decided that a further meeting should be held to thrash out practical points for the setting up of the scheme at an early date.

The meeting was attended by representatives of the Universities of Birmingham, Bristol, Cambridge, Durham, Glasgow, London, Manchester, Oxford, Sheffield, Wales, and the Imperial College of Technology and the University College of Nottingham.

Letters had been received from Queen's University, Ireland, and Liverpool University, expressing their sympathy with the scheme, and regretting their inability to be represented at the meeting.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, May 22, 1919.

Sir J. J. THOMSON, O.M., President, in the Chair.

THE following papers were read:—

"On the Structure of *Lysorophus* as Exposed by Serial Sections." By Prof. W. J. SOLLAS, F.R.S.

As the precise position of *Lysorophus*, regarded by Broom as the most interesting vertebrate fossil discovered for many years past, still remained open to discussion, some nodules containing its remains were placed in my hands for investigation by serial sections.

This work is now complete, and all the facts of the anatomy of the skull and vertebrae, and the main features of the shoulder girdle and fore limbs are exposed with a precision and wealth of detail only otherwise to be looked for in a recent skeleton.

It is now placed beyond question that *Lysorophus* belongs to an ancestral group of amphibians closely related to the Urodela.

Among the striking primitive characters it retains may be mentioned the presence of a basi-occipital and a supra-occipital bone, with a foramen in the former for the xiiith nerve, and possibly connected with this the presence of a large paired proatlas. There is also a separate opisthotic, and a pair of pillars, recalling the epipterygoids of the Chelonians, which may provisionally be termed ali-sphenoid.

The condylar articulation of the skull is of particular interest; while all the other vertebrae are amphicoelous, the first is opisthocelous and is swollen in front into an odontoid process, which plays against the nearly flat posterior face of the basi-occipital. The ex-occipitals are seated in part on the basi-occipital and in part on the first vertebra, thus forming with the basi-occipital a hollow joint (opisthocelous) in contrast to the procelous articulation of the reptilia.

The arch of the first vertebra and the face of the proatlas are closely applied to the back of the skull in a manner which recalls many fishes.

The hyoid (hypohyal and ceratohyal), and the branchial arches (cerato-branchial and epibranchial) are large and well ossified. The number of the branchial arches is at least three, more probably four.

"A Preliminary Study of the Energy Expenditure and Food Requirements of Women Workers." By O. ROSEN. HEIM.

Direct determinations (by the Douglas-Haldane method) of the energy expenditure of women were made during periods of rest, recreation, and work, the latter referring to work on the lathe. By means of the data obtained, an approximate estimate of the daily food requirements, expressed in calories, was arrived at on the basis of certain considerations set forth in the communication. The results agree with those of previous workers obtained by indirect statistical methods.

"Report on the Metabolism of Female Munition Workers." By M. GREENWOOD, C. HODSON, and A. E. TEBB.

Observations were made upon 43 women engaged upon 12 different processes in the manufacture of projectiles, the rate of metabolism being determined by the method of indirect calorimetry. Making the allowance for metabolic needs during non-working hours recommended by the Royal Society Food (War) Committee, the workers were found to fall into four classes, for each of which the daily requirements per average woman were 2530 calories, 2810 calories, 3200 calories, 3425 calories. The results were concordant with the inferences drawn from a study of food consumption in a large explosives supply factory during the war. The figures obtained in this experimental work were somewhat larger than those reached by Becker and Hämäläinen.

GEOLOGICAL SOCIETY.

Ordinary Meeting, May 7, 1919.

Mr. G. W. LAMPLUGH, F.R.S., President, in the Chair.

THE PRESIDENT said—Major R. W. Brock, formerly Director of the Geological Survey of Canada, was called upon last year to undertake on behalf of the War Office an arduous journey in Palestine, during which he had to devote particular attention to the Dead Sea region. At the request of the Officers of the Society, Major Brock has kindly undertaken to tell us something of his observations in the country. It is needless to say that the region is of surpassing interest to geologists, and I am sure that the Fellows will appreciate the opportunity of hearing how its remarkable features have impressed so acute and experienced a field-geologist.

Major REGINALD W. BROCK, M.A., F.G.S., then proceeded to deliver his lecture on the Geology of Palestine, his observations being summarised as follows:—

The following formations are recognised—

QUATERNARY.

- Alluvium. Dunes; Valley and Plains clay, and Silt; Desert Crust.
- Diluvium. Terrestrial: Lisan Formation (Jordan-lake-beds).
- Marine: Upper Calcareous Sandstone and Limestone. Lower Calcareous Sandstone.
- Heavy volcanic flows, basalts, ashes, tuffs, &c.

TERTIARY.

- Pliocene. Lacustrine.
- Eocene. Nummulitic Limestone.

MESOZOIC.

- Cretaceous. Upper: Senonian (Danian; Campanian; Santonian); volcanics, basalts.
- Lower: Nubian Sandstone; Jebel-Usdum formation (?)
- Jurassic. On Lebanon and Hermon only.

PALÆOZOIC.

Carboniferous. Possibly south-east of the Dead Sea.

Cambrian. Dolomite and sandstone.

PRE-CAMBRIAN.

Volcanics and arkose.

Red granites and porphyries.

Grey granites, gneiss, and crystalline schists.

The structure was shown to be that of a tableland bisected by a great rift-valley (graben), and flanked by a coastal plain. A section was exhibited illustrating East Jordanland acting as a horst; the boundary-faults of the Jordan Trench; the unequal sinking of the contained blocks; the western section of the tableland sunken with relation to the eastern, and thrown into an asymmetric anticline, the limbs of which rise in steps through monoclinical flexures or faults.

Lantern-slides were used to illustrate the character of the country and outstanding features in its geology, more particularly the following:—The dependence of the topography upon geological structure, slopes depending on the attitude of the rocks and elevation upon the raising or depressing of fault-blocks or on lava-flows; basins and sunken areas in the tableland; the scarps bounding the Jordan Trench, especially the western fault and fault-blocks in the Trench or against its walls that have not sunk equally with others; the upturned block of Jebel Usdum which, with the Dead Sea bottom and the block north of Jericho, indicates a median fault between the boundary-fault; the interbanding of the Jebel-Usdum salt with sandstone and shales that resemble Nubian Sandstone; the unconformity of the Jebel-Usdum formation with the Jordan lake-beds (Lisan formation), which with the chemical composition of the salt (lack of bromine, &c.) shows that it is not a Jordan lake deposit; high lake-terraces in the centre of the Trench, with corresponding ones north of Tiberias and south in the Araba Valley, showing that the Jordan lake stood 1400 feet above the present Dead Sea, and that there has been no marked warping since their formation; old gravel-filled cañons of the Arnon and Terka Main which prove that the level of the Dead Sea before Jordan-lake days stood at about its present level, and that climatic conditions must have been about the same, also that it did not long precede the Jordan lake; the Lisan formation of the Jordan lake-beds, thin layers of mechanical and chemical sediments veneered along the Jordan river with fluviatile clays; bad-land topography near the wadis and in the Lisan formation; narrow box cañons of the wadis in the Jordan Trench and the more open valleys above producing a sort of "hanging valley."

In the main, Blanckenborn's recent work was confirmed, in particular the fault forming the western border of the Trench and disturbances and sinking in the tableland; but new points were mentioned, such as the evidence of a median fault within the Trench; the sea-cliffs of Lisan and Jebel-Usdum; the wave-cut shelf and the salt of Jebel-Usdum; the tilting of the Jebel-Usdum block and its independence from and unconformity with the old lacustrine beds; lack of disturbance and of warping since their deposition; the age and former level of the Old Dead Sea and the recent rise in the present sea, the latter indicating an increase in moisture and not drier conditions as generally supposed.

A vote of thanks was unanimously accorded to Major Brock for his lecture.

ROYAL INSTITUTION.—A General Meeting of the Members of the Royal Institution was held on June 2. Sir James Crichton-Browne, F.R.S., Treasurer and Vice-President, in chair. Captain Ralph A. Bagnold, Mrs. Charles Cave, Mr. Edmund Davis, J.P., Miss Amelia D. Defries, Mr. William E. Schall, and Mr. Frank Twyman were elected members.

NOTES.

AN interesting paper on the "Occlusion of Hydrogen by the Metallic Elements," by Donald P. Smith, is given in the *Journal of Physical Chemistry* for March, 1919. The results of a very complete search of existing literature are embodied in tabular form, and the conclusion of the author that the capacity of a metal to occlude hydrogen is connected with its magnetic character is best given by the Summary that follows the paper:—"From a review of the literature relating to the occlusion of hydrogen by the metallic elements it is shown that the resulting alloys are clearly to be distinguished from other types of binary hydrogen compounds, and that the metals which form the alloys probably occupy a definite region in the periodic table of Werner. The metals of this region are classified into those which do, and those which do not, occlude in a degree measurable by the ordinary volumetric method. From a comparison with magnetic data it is shown that the occluding and non-occluding elements, excepting copper, rhodium, and thorium, are identical with those for which the specific magnetic susceptibility possess a value respectively greater or less than about $\pm 0.9 \cdot 10^{-6}$ at room temperature. It is concluded that the capacity of a metal to occlude hydrogen in large degree is an accompaniment of strongly magnetic character."

THE "TANK."—We are indebted to Major-General E. D. Swinton for an account of the origin of this contrivance about which so much has been said and written, and which undoubtedly contributed largely to the successful termination of the war. The account was given at an informal dinner following the general meeting of the Institute of Mining and Metallurgy on April 10 last. We quote the Major's own words:—"In July, 1914, Mr. Marriott wrote from Antwerp—where his job at the moment was trying to find out some cheap and efficient form of transport across rough country for mining purposes. He knew all about rope railways, telpherage, narrow-gauge railways, and so on, and informed him that in Antwerp he had seen an American caterpillar tractor which would go over rough country and climb 'like hell.' This, it must be remembered, was before the war. He (General Swinton) happened to be in a position then when he could approach different departments; in vulgar language he was a sort of Buttinski, and he was able to go to the War Office and the Admiralty and tell the people concerned that there was an American tractor in Antwerp which would, in the coarse words of his friend, 'climb like hell,' and that it was up to them to investigate it for tractive purposes. The machine referred to was the Holt tractor. Shortly after that he had gone out to the war, as he had said just now, as a journalist, and his position gave him an opportunity of seeing and learning a lot. It was then that he became convinced that a machine which could climb like hell was a thing not to be lost sight of, and if it could be developed or improved into a bullet-proof machine which could climb 'to beat hell' they had something which might meet the German machine guns."

At a recent meeting of the Society of Public Analysts and other Analytical Chemists a paper was read by Helen Masters, B.Sc., on "Soluble Lead in the Glaze of Casseroles." Attention was drawn to the extended use of glaze vessels for culinary purposes and to the danger that food cooked in such vessels might become contaminated with lead. In Germany the sale of vessels which yield any soluble lead on boiling for thirty minutes with a 4 per cent solution of acetic acid is prohibited. Experiments with various glazed vessels show that in some cases a considerable amount of lead can be extracted from the glaze, not only by the action of 4 per cent acetic acid, but also by the action of more dilute solutions of organic acids, e.g., 1 per cent acetic, citric, or malic acid. In some cases as much as from 2 to 4 mgrms. of lead

monoxide per square decimetre was extracted by a 1 per cent acetic acid solution in thirty minutes, and in an exhaustive experiment of this kind as much as 28.7 mgrms. of lead monoxide per sq. dm. was extracted by twelve successive boilings. The danger of the use of such vessels is very real, and manufacturers would do well to have reliable tests made of their wares so as to avoid the use of soluble glazes; the expense would probably be well repaid by marking their wares with a guarantee of their insolubility.

WE have received a copy of the first number of a new publication, the *Italian Gazette*, a financial, commercial, and economic review, a quarterly journal, edited by Roberto Lombardo, with Edward Storr, as sub-editor; published at Piazza Cavour 17, Rome. The matter opens with a message of appreciation from the British Ambassador, Sir Rennell Rodd, and the object is to improve and strengthen the relations of sympathy and friendship between England and Italy that have become so apparent during the War. In a brilliant introductory article by Luigi Luzzatti the need for an intimate friendship between Italy and England is developed. Other articles on financial and commercial matters by prominent Italians appear, and in all of them there is to be noticed a sincere desire for the friendly relations between us to be expanded for our mutual benefit, and an avowal of their distrust of Teutonic methods in commercial and other circles that has been brought home to them as to other nations by recent developments. We wish the new publication every success. Our only regret is that it is not to appear at more frequent periods than once a quarter.

NOTES FROM FOREIGN SOURCES

Stability of Javel Extracts.—M. Fonze-Diacon.—Javel extracts, when kept, lose considerable quantities of active chlorine, the loss being caused principally by the action of light and the author has made a study of the course of the reaction and the conditions which may lead to its reduction to a minimum. Eight samples were exposed to the action of diffused light by putting them before a well lighted window on which direct sunlight was not falling; two were placed in flasks made of yellow glass, one of a much darker shade than the other, and the six others in white glass. The chlorine was determined at intervals of time extending over about four months, and it was found that even in that time the loss of chlorine in the dark yellow flask was very small; in the less deeply coloured glass it was rather greater and still more marked in the white flasks. The greater the proportion of active chlorine the greater the loss, and after four months' exposure to the action of light extracts which originally contained very different amounts gave results which approached a common limit. If the initial amount of active chlorine present is about 5 grms. per 100 cc., and if the extracts are kept in dark yellow flasks, they may be regarded as unaltered at the expiration of several months.—*Bull. Soc. Chim. de France*, 1919, xxv. xxvi., 206.

Analysis of Antimony Salts.—Various methods have been suggested for the analysis of antimony sulphide, which may contain free sulphur, antimonio acid, antimonates, red antimony sulphide, antimony oxysulphides, or calcium sulphate. The oldest methods of determining the amount of free sulphur depended upon the extraction of it by carbon disulphide, using a Soxhlet's apparatus, and it has recently been found that the pentasulphide is practically unattacked in the cold, and even on warming only about 0.4 per cent is reduced. Benzene or acetone can be used as solvent, but if benzene is used the pentasulphide must previously be thoroughly dried. Acetone is not to be recommended, for it dissolves a small quantity of the sulphide in addition to the free sulphur. Another

method of determining the impurities depends upon the fact that antimony pentasulphide is completely soluble in warm ammonia, and the other substances present can be filtered off and determined in the usual way. To estimate the total sulphur the sulphide can be dissolved in a solution of pure potash and then subjected to the action of chlorine, when all the sulphur is transformed into sulphuric acid and the antimony into antimonic acid. Fuming nitric acid can also be used to convert the sulphide into sulphate, which can be estimated as barium sulphate in the usual way, and hydrogen peroxide acts similarly. If the sulphide is dissolved in pure sodium sulphide the percentage of antimony present can be determined by electrolysis, platinum electrodes being employed; but this process cannot be recommended, for the values obtained are always too high. By treating a solution of the sulphide with soda and hydrogen peroxide and adding alcohol, a precipitate of sodium antimonate is obtained after thirty-six hours' standing. From the weight of this precipitate the amount of antimony present can be deduced. In an alternative process the antimony is determined as tetroxide, Sb_2O_4 . A given weight of the sulphide is heated over a water-bath with hydrochloric and nitric acids. The solution is evaporated to dryness, taken up with hydrochloric acid, diluted, and filtered. The precipitate consists of silica and calcium sulphate. The antimony is contained in the filtrate, which is decomposed by HCl, and oxidised to give Sb_2O_4 .—*Revue des Produits Chimiques*, 1919, xxii., 199.

Determination of Arsenic in Volatile Cacodylic Compounds.—L. C. Maillard.—Cacodyl and its compounds readily combine with oxygen to give cacodylic acid, which is a very stable derivative in ordinary conditions. It is non-volatile, has no smell, and is not toxic. For the purposes of analysis the best oxidising agent to use is persulphuric acid, employed in the form of ammonium persulphate. To extract the arsenic from the cacodylic acid the latter is attacked with a mixture of nitric and sulphuric acids, the excess of nitric acid is driven off by heating, and the arsenic is precipitated in the diluted solution as sulphide, and weighed either as sulphide, or as arsenic acid, or as magnesium pyroarsenate. Even in the case of a long series of operations, when an accumulation of errors might be feared, the author has found by a control experiment that this method gives excellent results in determining arsenic in volatile substances of the cacodyl series, and it is possible that it may be applicable to the case of other organic compounds containing arsenic of more or less comparable composition.—*Bull. Soc. Chim. de France*, 1919, xxv.-xxvi., 192.

MEETINGS FOR THE WEEK.

Saturday, June 7.

Royal Institution, 3. "The Italian Front," by J. M. Price.

Wednesday, June 11.

Conjoint Board of Scientific Societies, 5. (At Royal Society, Burlington House).

Thursday, June 12.

Royal College of Physicians, 5. (Croonian Lecture). "The Significance of the Cerebral Cortex," by Prof. C. Elliot Smith.

Friday, June 13.

Physical Society, 5. "Comparison of the Wave-form of the Telephone Current produced by a Thermal Detector and a Rectifier in the Heterodyne Reception," by V. van der Pol. "Magnetic Properties of Varieties of Magnetite," by E. Wilson and E. F. Herroun.

Saturday, June 14.

Biochemical Society, at Rothamsted Experimental Station, Harpenden.

Chemist, demobilised, three years' Technical
College training and one year works experience, in order to regain experience, lost Army service, would communicate with Analyst of extensive practice with view to Post as Pupil Assistant for limited period.—Address, R. B., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Chemist, three years' experience in large Tar
Products Works before taking active service, now demobilised, desires Employment in London or the Provinces.—Address, T. T., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Chemist required at once for Analysis of
Chrome Steel and General Metallurgical products. State experience and salary.—Address, C. S., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Junior Assistant Chemist wanted for the Full
Research Laboratory. One preferred with B.Sc. Degree, but not absolutely essential. Should have good knowledge of Geology and Palaeobotany. State particulars of training and experience, age, and salary required.—Address, F. R., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Metallurgical and Research Chemist (Univer-
sity training and extensive Works experience) will soon be free to accept another Engagement as such, or any position of trust where organising abilities and Technical knowledge are desired, at home or abroad. During war was Chemist in charge of large Engineering firm.—In first place please address communications to "L," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

University man (Demobilised Officer), first
class in Chemistry and Mathematics at London Inter.B.Sc., and excellent testimonial from his Professor, desires situation, either of Secretarial nature or in some capacity utilising above qualifications.—Address, U. M., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

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Chemistry and Engineering practice, desires Situation at living wage with Chemical Engineering firm, or Assistantship in Works Laboratory of progressive firm which appreciates intelligent and willing service.—Address, Sharpe, 7, Toll Road, Kincardine-on-Forth.

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ducts, well connected amongst important importation firms of Bordeaux and South-West of France for SULPHATE OF COPPER, requires Agency for Bordeaux. Highest references.—Write to Box 8059, Agence Havas, 105, Cheapside, London, E.C. 2.

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THE CHEMICAL NEWS

VOL. CXVIII., No. 3087.

RESEARCHES IN OPTICAL ACTIVITY.*

PART I.—THE TEMPERATURE-ROTATION CURVES FOR THE TARTRATES AT LOW TEMPERATURES.

By T. S. PATTERSON, D.Sc., Ph.D., Waltonian Lecturer and Lecturer in Organic Chemistry, University of Glasgow, and K. L. MOUDGILL, B.Sc., late Robert Donaldson Scholar, University of Glasgow.

In some previous papers by one of the present authors it has been shown, by piecing together evidence obtained in various ways, that if the rotation of such a substance as

been shown by Walden (*Ber.*, 1905, xxxviii., 371) that cinnamic aldehyde has a very marked effect upon the rotation of ethyl tartrate and of methyl malate, the mere numerical values being greater than those recorded for either of these active substances in any other solvent, on which account we were anxious to ascertain whether the behaviour in the former case fitted in with the views previously developed or not.

A solution of ethyl tartrate in cinnamic aldehyde, $p=9.64$ (p =grms. active substance per 100 grms. of solution), was therefore prepared, and the rotation examined for six colours of light. Three of these, yellow, green, and violet, were obtained direct from a mercury arc lamp, whilst the other three, dark red (r_1), red (r_2), and blue, which correspond to three fainter lines in the mercury arc, were obtained from a Nernst lamp by a method which has been described elsewhere (*Journ. Chem. Soc.*, 1916, cix., 1144). The wave-lengths of the light used were as follows:—

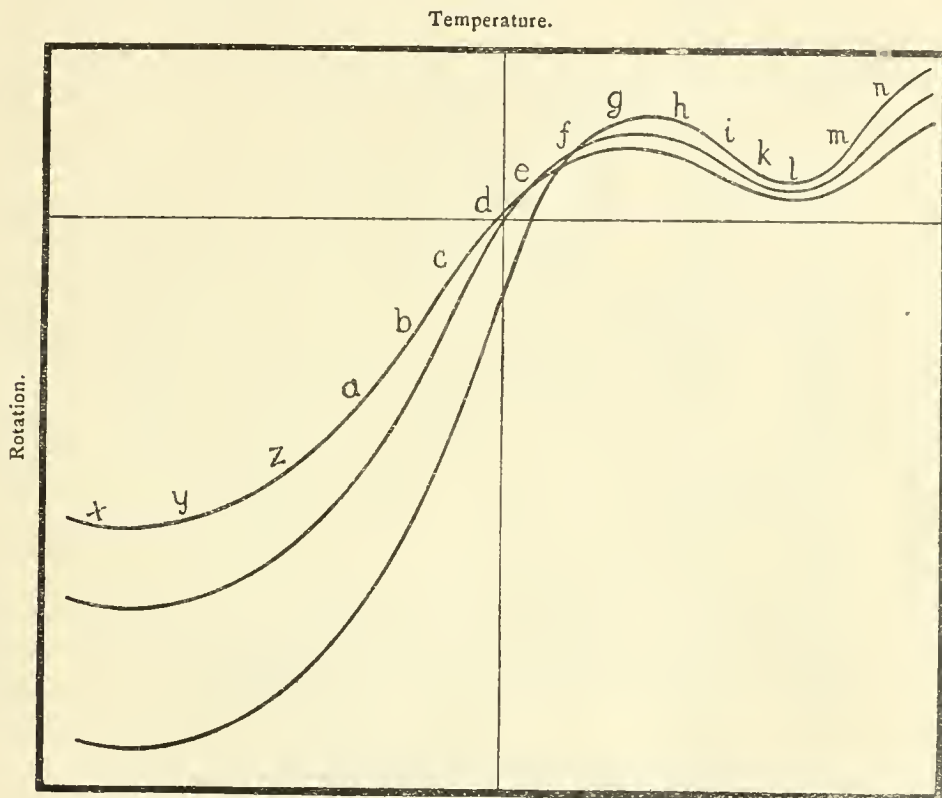


FIG. 1.—General Temperature-Rotation Curves for Tartrates.

ethyl tartrate could be examined for different colours of light over a sufficiently wide range of temperature, the graphs would have the appearance shown in Fig. 1; they have been traced up to the present from about the region a to the region n . In the paper now submitted an attempt has been made to follow the trend of these T—R curves towards low temperatures, adopting the same method as before. In the following experiments a start has been made in this direction, but before passing on to our primary purpose we thought it worth while to investigate one rather striking instance of solvent effect connected with the high temperature end of the diagram. It has

r_1	r_2	y	g	b	n
6716.3	6234.3	5790.3	5460.7	4959.7	4358.3

It will be noticed that the rotations at low temperatures are great, and that as the temperature rises the rotation diminishes, which was in accordance with expectation. The T—R curves for this solution are shown in Fig. 2, and are there contrasted with those for ethyl tartrate in quinoline $p=13.601$ (*Journ. Chem. Soc.*, 1916, cix., 1145, 1151). The curves are, on the whole, similar, but those for the cinnamic aldehyde solution lie higher on the diagram than those for the quinoline solution. In quinoline a minimum is apparent, but in cinnamic aldehyde the curves are only tending towards a minimum, which would lie at a distinctly higher temperature than could, meantime, be reached. Now

* Abridgment of a paper in the *Proceedings of the Royal Society of Edinburgh*, 1918-19, xxxix., 18—34.

it has been suggested in recent papers that the influence of a solvent should be measured, not so much by the actual value of the rotation in given circumstances, as by the effect which the solvent produces on the whole family of T—R curves. If this be so—and there is much evidence in favour of the idea—quinoline must be regarded as a more powerful solvent for this ester than is cinnamic aldehyde, since the shifting of the T—R curve is apparently much greater in the former than in the latter case, and it is at least quite possible, indeed it is very probable, that if the quinoline solution were examined at lower temperatures

directly at low temperatures; but this procedure presents a number of difficulties such as the likelihood of solidification of the active substance or of the solvent, or the difficulty of obtaining and maintaining low temperatures. Secondly, the active compound may be dissolved in some solvent which brings into the region of ordinary temperatures the T—R curves, which, in the homogeneous substance, could only be directly observed at very low temperatures. Thus in the case of ethyl tartrate it has already been shown (*Journ. Chem. Soc.*, 1908, xciii., 360; Winther, *Zeit. Phys. Chem.*, 1907, lx., 578) that in

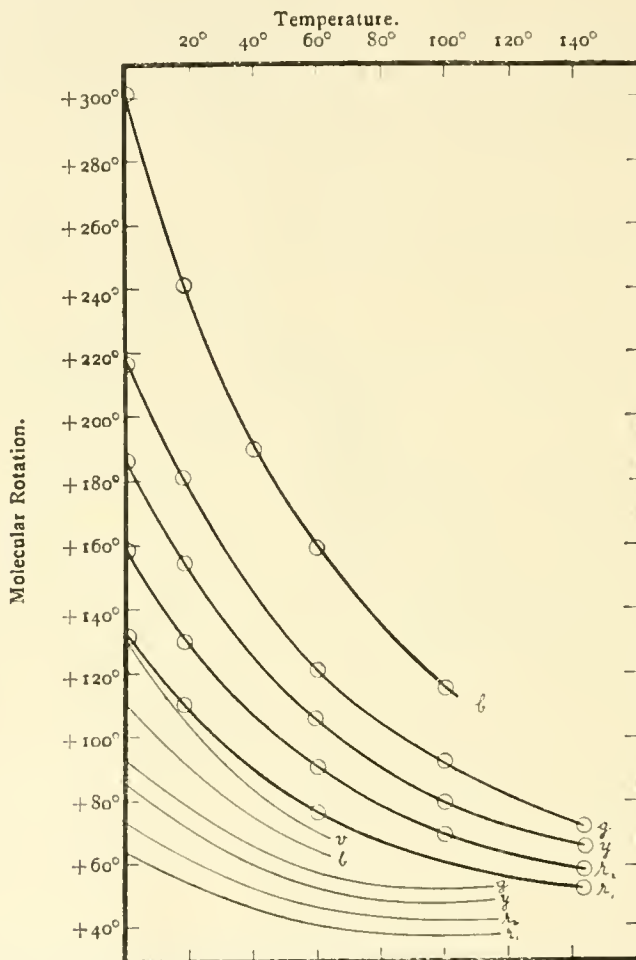


FIG. 2.—Temperature-Rotation Curves for Ethyl Tartrate in Cinnamic Aldehyde, $p = 9.64$ (heavy lines), and in Quinoline, $p = 13.60$ (thin lines).

than those for which the diagram applies, the quinoline curves would rise to higher values than those for cinnamic aldehyde. This is also in agreement with the fact that whereas C—R (concentration-rotation) curve for ethyl tartrate in quinoline shows a pronounced maximum (*Journ. Chem. Soc.*, 1909, xcv., 322), Walden's results for ethyl tartrate in cinnamic aldehyde give only a very slight indication of the occurrence of this phenomenon in dilute solution.

We may now turn to the question with which this paper is primarily intended to deal, namely, the course of the T—R curves for tartrates at low temperatures. There are various ways of investigating the problem. Firstly, a substance, homogeneous or in solution, can be examined

ethylene bromide the rotation is very considerably depressed, wherefore most probably, in this particular solvent, the whole T—R curve is displaced towards the right of the diagram—that is, in the direction of high temperatures; or, to put it otherwise, ethylene bromide brings into view, at the ordinary temperature, the part of the diagram *a b c* (Fig. 1), which, in homogeneous ethyl tartrate, could only be observed at decidedly lower temperatures. The behaviour of ethyl tartrate in ethylene bromide at moderate temperatures ought therefore to reveal the behaviour of the homogeneous ester at temperatures lower still. Thirdly, the behaviour of some related substance can be studied either in the homogeneous condition or in solution. Thus in passing from

ethyl tartrate to isobutyl tartrate—a slight change of constitution—the general T—R curves are slightly displaced towards the left, towards lower temperatures; whereas on converting ethyl tartrate into ethyl diacetyl tartrate—a considerable change of constitution—the displacement of the general T—R curves is very much greater and is in the opposite direction.

Applying, to begin with, the second of these methods, ethyl tartrate was examined in ethylene bromide solution. Unfortunately, in attempting to get readings at as low a temperature as possible, the solution was cooled rather too

region of minimum rotation, and since ethylene bromide is either the most powerful, or almost the most powerful, depressing solvent known for this ester, we were forced to turn next to the third method of investigation, namely, that of examining the T—R curves of some other tartrate, in which there is reason to suppose that the change of constitution has brought about a considerable shifting of the family of T—R curves.

Now it has been shown by Frankland and Wharton (*Journ. Chem. Soc.*, 1896, lxi., 1587, also 1309) that the rotation, for yellow light, of ethyl dibenzoyltartrate

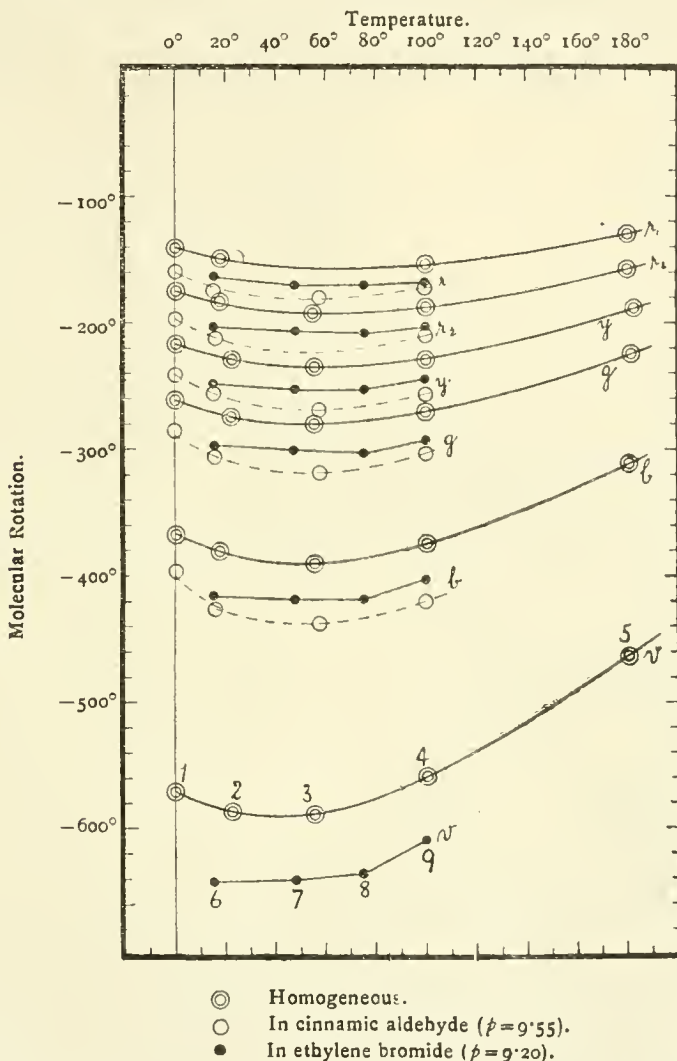


FIG. 3.—Temperature-Rotation Curves for isoButyl Dibenzoyltartrate in various Solvents.

far, so that the solvent crystallised out and spoiled the experiment at an early stage. Nevertheless it was found that the rotation for violet is, in the absolute sense, very much lower than for the other colours examined, and that the rotation increases rapidly with rise of temperature, so that the effect of this solvent is very much the opposite of that of cinnamic aldehyde, whence it may be concluded that the former is represented by the part *bc* of the general curves (Fig. 1), whereas the latter is represented by the region *h i k*. But it is clear that the depressing influence of ethylene bromide is not sufficient to take us into a

exhibits a distinct minimum rotation at 60.4° ; moreover, this rotation is low in value ($[\alpha]_D^{18} = -59.36^\circ$), and it seems clearly possible that the T—R curves for this ester at ordinary temperatures represent the behaviour of ethyl tartrate—the parent ester—at very much lower temperatures. The examination of an active substance for a single colour of light can only yield an indication in regard to this question, but an examination of the T—R curves for various colours of light makes a definite decision possible. Thus if, for example, the minimum in ethyl dibenzoyltartrate correspond to the minimum which exists in ethyl

tartrate at about 180° , namely, to the region $k l m$ in Fig. 1, then we should expect the dispersion to be the same in both cases, namely, positive; the rotation for violet should be greater, in an absolute sense, than for red. But if the minimum were such as is to be expected from a continuation of the ethyl tartrate curves towards low temperatures, or for the curves for ethyl tartrate in ethylene dibromide, the rotation for red might be expected to have a higher absolute value than the rotation for violet, the dispersion then being negative. In this way it is possible to decide to which region of the ethyl tartrate curves those for ethyl dibenzoyltartrate correspond. Instead, however, of the ethyl derivative, we prepared isobutyl dibenzoyl-

neighbourhood of zero rotation, the observed behaviour is, so far, in agreement with our views. It would obviously, however, be of interest to examine these curves towards the right-hand side of the diagram, and, in the hope of being able to shift them far enough to link them up definitely with those for ethyl tartrate or isobutyl tartrate, isobutyl dibenzoyltartrate was examined in ethylene bromide and in cinnamic aldehyde solutions, the curves obtained being also shown in the diagram in Fig. 3. But in this we were disappointed, for although the solvents altered the rotation to some extent, the change is not very great. In cinnamic aldehyde the general character of the curves appears to be almost the same as in the homo-

This Diagram is for Green and Violet, the Reference Colour being Green.

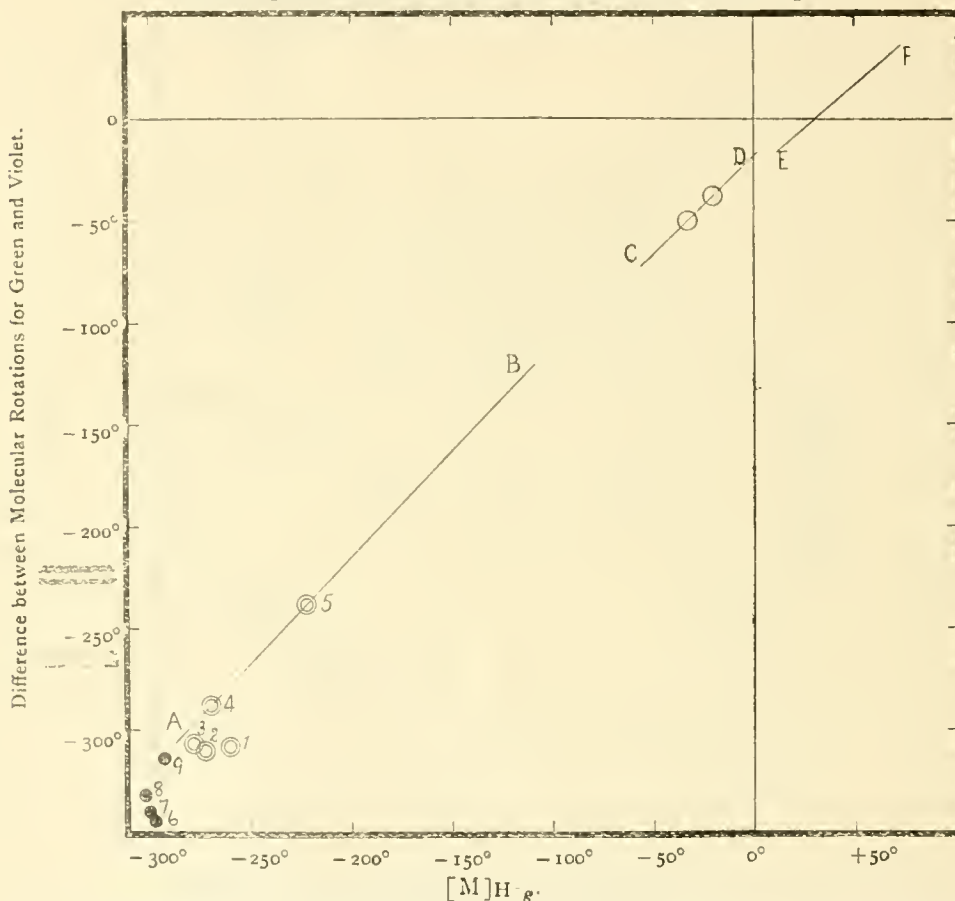


FIG. 4.—Characteristic Diagram for Ethyl Tartrate (Homogeneous and in Ethyl Bromide, $p=9.84$), and for isoButyl Dibenzoyltartrate (Homogeneous and in Ethyl Bromide, $p=9.20$).

tartrate and examined its rotation over a range of temperature in the homogeneous condition as well as in solution in cinnamic aldehyde and in ethylene bromide. The results are plotted in Fig. 3, and it will be observed that the form of the curves is in agreement with the second suggestion made above. The absolute value of the rotation diminishes from red to violet; the dispersion is negative. There is a distinct minimum in each of the curves, and this minimum passes slightly towards lower temperatures as the refrangibility of the light becomes greater, although the displacement is comparatively small. The rotation tends to rise somewhat rapidly as the temperature increases; and since the appearance of the curves is not inconsistent with the possibility of intersection in the

homogeneous ester; in ethylene bromide there appears to be some slight difference in form, which we think can hardly be due to experimental error, but to which in the meantime we can do no more than direct attention.

Since the T—R curves for homogeneous isobutyl tartrate and isobutyl dibenzoyltartrate thus show directly no common feature such as, for example, a similar maximum or minimum, or the intersection which is known as anomalous rotation-dispersion, their relationship is not so obvious as might otherwise be the case. That they are connected with one another is rendered clearer by the application of Armstrong and Walker's characteristic diagram (*Proc. Roy. Soc., A*, 1913, lxxxviii., 392), the interpretation of which, from the point of view of the

T—R curves, has already been discussed by one of us (*Journ. Chem. Soc.*, 1916, cix., 1180, 1195). From what was there said it is to be expected that if the T—R curves for isobutyl dibenzoyltartrate and those for isobutyl tartrate or ethyl tartrate are related, as suggested above, then the experimental data corresponding to the region $y \approx a b c$ of Fig. 1 should lie along a common line in the characteristic diagram. The points on the curve for ethyl tartrate in ethylene bromide, which clearly belong to this region, should lie along the same line, whereas points belonging to the T—R curves for isobutyl dibenzoyltartrate at temperatures below that at which the minimum occurs—that is to say, in the region of x (Fig. 1)—should not necessarily be expected to lie along the same line on the characteristic diagram. It will be seen from Fig. 4 that this is actually the case.

(NOTE.—The diagram is drawn according to the author's modification of Armstrong and Walker's method. Rotation values for Hg_g are plotted along the horizontal axis (the reference line), the differences between the rotation values for Hg_v and Hg_g , and Hg_v and Hg_g respectively being then plotted, according to sign, vertically above or below the corresponding values for Hg_g . The actual rotation value at any point on the diagram is the horizontal distance from the zero-point, plus (or minus) the vertical distance from the reference line.—See *Journ. Chem. Soc.*, 1916, cix., 1181).

The points marked 1, 2, and 3 (shown also in Fig. 3), for isobutyl dibenzoyltartrate, obviously do not lie on the line AB in Fig. 4. But the points 4 and 5, which are on the part of the curve corresponding to xy in Fig. 1 do lie on the line AB , and this has almost the same direction as that joining the two points for ethyl tartrate in ethylene bromide $c d$, both being close to that for ethyl tartrate itself, $e f$. Considering that we are comparing the behaviour of ethyl tartrate with that of the dibenzoyl derivative of a homologous ester, the agreement is, on the whole, very satisfactory, and it may therefore be concluded that the curves in Fig. 1 represent the influence of temperature-change upon the derivatives of tartaric acid generally; that on extending the diagram towards the left a very deep minimum is reached in the neighbourhood of low temperatures.

A slightly different way in which the connection between isobutyl dibenzoyltartrate and the ethyl tartrate curves might be shown is as follows:—It is reasonable to suppose that if this relationship exists, the dispersion coefficient should remain constant with varying circumstances, and should be the same for both esters. But it has been shown in a recent communication (*Journ. Chem. Soc.*, 1916, cix., 1183) that constancy can be expected only if the dispersion coefficients be calculated from what was called a rational zero. The rational zero (taking molecular rotations) for the Hg_g and Hg_v T—R curves—i.e., the rotation value at their point of intersection—for homogeneous ethyl tartrate was found to be 29.4° , and when the dispersion ratio was calculated from this rotation value as zero the number 2.0939 was found (*Ibid.*, 1191). The rational zero for the green and violet lines for isobutyl dibenzoyltartrate cannot meantime be determined directly, but assuming the dispersion ratio to remain constant over the requisite interval, the rational zero can obviously be calculated from the rotation data at 100° and 182° , which are as follows:—

Isobutyl Dibenzoyltartrate.

Temperature.	100° .	182° .
$[M]_v$	 -559°	-463°
$[M]_g$	 -271°	-223°

Since the dispersion coefficients at these two temperatures should, by hypothesis, be the same, we must have—

$$\frac{559^\circ + x^\circ}{271^\circ + x^\circ} = \frac{463^\circ + x^\circ}{223^\circ + x^\circ},$$

where x° is the value of the rational zero. From this

equation $x^\circ = 17^\circ$, and setting this value in either of the above expressions, the dispersion coefficient 2.00 is obtained, very nearly the same as that of ethyl tartrate for these two colours of light. Again, taking the data for ethyl tartrate in ethylene bromide, we should have in a similar manner—

$$\frac{81^\circ + x^\circ}{32.86^\circ + x^\circ} = \frac{58.06^\circ + x^\circ}{20.53^\circ + x^\circ},$$

from which $x^\circ = 18.7^\circ$, almost the same value as found for isobutyl dibenzoyltartrate, and, accepting this as the rational zero, the dispersion ratio is 1.96 , again much the same as in homogeneous ethyl tartrate for the same two colours of light.

Organic Chemistry Department,
University of Glasgow.

GALLIUM.*

By L. M. DENNIS and J. ALLINGTON BRIDGMAN.

(Continued from p. 272)

Preliminary Experiments upon the Determination of Gallium, Indium, Zinc, and Aluminium in the presence of One Another.

SOLUTIONS of salts of gallium, zinc, indium, and aluminium of known concentrations were prepared as follows:—

A solution of gallium sulphate was made in the manner above described, and its concentration was ascertained by precipitation of gallium by sodium sulphite.

Indium chloride that had been prepared by Mathers (*loc. cit.*) was dissolved in water, and measured portions of this solution were boiled with a slight excess of ammonium hydroxide. The precipitated indium hydroxide was ignited to the oxide, which was then allowed to cool, was moistened with nitric acid, was reignited, and was weighed as In_2O_3 .

Pure zinc sulphate was dissolved in water, and the strength of the solution was determined by precipitation with potassium mercuric thiocyanate.

The concentration of a solution of aluminium sulphate was determined by the usual method of precipitation with ammonium hydroxide.

Portions of these four solutions, carefully measured from burettes, were used to prepare the mixtures that were employed in the study of the analytical separation and determination of the four elements.

Separation and Determination of Gallium and Indium.

Solutions that contained known amounts of gallium and indium were each diluted to 200 cc. A small amount of hydrochloric acid was added to each solution, and a solution of sodium hydroxide was run in until the liquid was neutral. 1.5 grms. of sodium hydroxide in excess was then added and the solution was boiled for several minutes. The resulting precipitate of indium hydroxide was collected on a filter and washed, and was then redissolved in hydrochloric acid, and the indium reprecipitated by again boiling with an excess of 1.5 grms. of sodium hydroxide. This precipitate was removed by filtration and was washed; it was then dissolved in hydrochloric acid, and the indium was determined by precipitation with ammonium hydroxide in the manner previously described. The alkaline filtrates from the two precipitations of indium were combined and were acidified with hydrochloric acid. The gallium was precipitated by sodium sulphite, the precipitate was collected on a filter and washed, was dissolved in hydrochloric acid, and the gallium

* This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by J. Allington Bridgman in partial fulfilment of the requirements for the degree of Doctor of Philosophy. From the *Journal of the American Chemical Society*, xl, No. 10.

was reprecipitated with sodium sulphite and was finally weighed as the oxide.

TABLE VIII.—*The Separation of Gallium from Indium.*

	1.	2.	3.
Weight of Ga_2O_3 taken (grm.)	0.0828	0.0828	0.0828
Weight of Ga_2O_3 found (grm.)	Not det.	0.0834	0.0828
Weight of In_2O_3 taken (grm.)	0.0647	0.0647	0.0647
Weight of In_2O_3 found (grm.)	0.0660	0.0662	0.0676

The results for gallium are satisfactory, but those for indium are somewhat high. Later determinations of indium in the presence of gallium by this method yielded, however, very satisfactory results. (See Table XV.)

Separation and Determination of Gallium and Zinc.—Solutions containing known amounts of gallium and zinc were diluted to about 200 cc., and 2 cc. of sulphuric acid was added to each solution. The zinc was precipitated from these solutions by potassium mercuric thiocyanate. Ten cc. of hydrochloric acid was added to each filtrate, and the mercury in the filtrate was precipitated by hydrogen sulphide. After removal of the mercuric sulphide by filtration the solutions were boiled to remove hydrogen sulphide, and the gallium was precipitated by sodium sulphite. It will be seen that the results for both gallium and zinc by this method are quite satisfactory.

TABLE IX.—*The Separation of Gallium from Zinc*

	1.	2.
Weight of zinc taken (grm.)	0.0939	0.0939
Weight of zinc found (grm.)	0.0929	0.0937
Weight of Ga_2O_3 taken (grm.)	0.0828	0.0828
Weight of Ga_2O_3 found (grm.)	0.0823	0.0830

Separation and Determination of Gallium and Aluminium.

Solutions of salts of gallium and aluminium of known concentration were prepared, and the aluminium was precipitated as a hydrated chloride (Dennis, *Zeit. Anorg. Chem.*, 1895, ix., 339) by a modification of the method of Gooch ("Methods in Chemical Analysis," 1912, p. 214).

In Determination No. 1 (see Table X.) 60 cc. of hydrochloric acid was added to the solution containing gallium and aluminium, and 60 cc. of ether was then added. The flask was immersed in cold water and the liquid was saturated with hydrogen chloride. The resulting precipitate of hydrated aluminium chloride was filtered on a Gooch crucible and was washed with a mixture of 30 cc. of hydrochloric acid and 30 cc. of ether, which had been saturated with hydrogen chloride. The precipitate was then dissolved in water and the aluminium was determined by precipitation with ammonium hydroxide. A small amount of sulphuric acid was added to the filtrate from the precipitation of aluminium chloride, and the liquid was then heated until the ether and most of the hydrochloric acid had been driven off; the gallium in the solution was then thrown down by sodium sulphite.

In Determination No. 2 only 25 cc. of hydrochloric acid and 25 cc. of ether were added before the solution was saturated with hydrogen chloride. A mixture of 25 cc. of hydrochloric acid and 25 cc. of ether, saturated with hydrogen chloride, was used to wash the precipitate.

TABLE X.—*The Separation of Gallium from Aluminium.*

	1.	2.
Weight of Al_2O_3 taken (grm.)	0.0841	0.0841
Weight of Al_2O_3 found (grm.)	0.0831	0.0825
Weight of Ga_2O_3 taken (grm.)	0.0828	0.0803
Weight of Ga_2O_3 found (grm.)	0.0844	0.0098

These results were not satisfactory, but further experience with the method enabled us to obtain quite accurate analyses by this method. (See Table XVII.)

Separation and Determination of Gallium, Indium, and Zinc. First Method.—Solutions that contained known amounts of gallium, indium, and zinc, gallium preponderating, were diluted to about 100 cc. Zinc was

precipitated by the addition of 25 cc. of potassium mercuric thiocyanate. After several hours' standing the precipitate was removed by filtration and the mercury in the filtrate was thrown down by hydrogen sulphide. The filtrate from this last filtration was boiled to remove hydrogen sulphide, and the indium and gallium were then separated and determined by the method previously described.

TABLE XI.—*The Separation of Gallium, Zinc, and Indium. First Method.*

	1.	2.
Weight of Ga_2O_3 taken (grm.)	0.0828	0.0828
Weight of Ga_2O_3 found (grm.)	0.0833	0.0833
Weight of zinc taken (grm.)	0.0038	0.0188
Weight of zinc found (grm.)	0.0041	0.0196
Weight of In_2O_3 taken (grm.)	0.0065	0.0129
Weight of In_2O_3 found (grm.)	0.0030	0.0075

The results for gallium were quite satisfactory, but those for zinc were high and those for indium were quite low. This may have been due to the presence of indium either in the precipitate of zinc mercuric thiocyanate, or in the precipitate of mercuric sulphide when the mercury is removed from the filtrate from the zinc precipitation. To throw light upon this point a solution that contained only indium and zinc was prepared and the zinc was precipitated as zinc mercuric thiocyanate. The excess of mercury was removed from the filtrate by hydrogen sulphide and the indium was precipitated by ammonium hydroxide.

TABLE XII.—*The Separation of Zinc and Indium.*

Weight of zinc taken (grm.)	0.0939
Weight of zinc found (grm.)	0.0969
Weight of In_2O_3 taken (grm.)	0.0649
Weight of In_2O_3 found (grm.)	0.0494

The result for zinc was quite high, and the precipitate of zinc mercuric thiocyanate was found to contain indium when examined before the spectroscope. This method, therefore, does not furnish a satisfactory means of determining zinc and indium in the presence of each other.

Second Method.—Solutions containing known amounts of gallium, indium, and zinc were prepared, and the indium was separated and determined by double precipitation with sodium hydroxide in the manner described previously. The alkaline filtrates from this double precipitation were combined, and the solution was neutralised with sulphuric acid. The zinc in this solution was determined by precipitation with potassium mercuric thiocyanate. The mercury in the filtrate from this precipitate was removed by hydrogen sulphide, and the gallium in the filtrate was determined by double precipitation with sodium sulphite (see ante).

TABLE XIII.—*The Separation of Gallium, Zinc, and Indium. Second Method.*

No.	Wt. of Ga_2O_3 taken. Grm.	Wt. of Ga_2O_3 found. Grm.	Wt. of zinc taken. Grm.	Wt. of zinc found. Grm.	Wt. of In_2O_3 taken. Grm.	Wt. of In_2O_3 found. Grm.
1.	0.0828	0.0813	0.0186	0.0171	0.0130	0.0129
2.	0.0828	0.0827	0.0367	0.0337	0.0323	0.0318
3.	0.0828	0.0821	0.0939	0.0926	0.0647	0.0650
4.	0.0828	0.0817	0.0075	0.0049	0.0065	0.0063
5.	0.0083	0.0079	0.0939	0.0944	0.0323	0.0335
6.	0.0828	Not det.	0.0188	0.0161	0.0130	0.0120
7.	0.0083	0.0061	0.0939	0.0942	0.0194	0.0195
8.	0.0083	0.0085	0.0075	0.0050	0.0647	0.0680

In Determinations 3, 5, and 7 an excess of 3 grms. of sodium hydroxide instead of the usual amount of 1.5 grms. was employed for the first precipitation of indium hydroxide. In Determinations Nos. 1 and 2 the precipitated indium hydroxide was dissolved in hydrochloric acid. In the other determinations it was dissolved in sulphuric acid.

It was found that in some cases zinc was present in the filtrate from the final precipitation of indium by ammonium hydroxide. Consequently, in all of the determinations except Nos. 1 and 2 this filtrate was treated with potassium mercuric thiocyanate, and any precipitate that formed was added to the main precipitate of zinc mercuric thiocyanate. An examination of the table will show that the results for gallium and indium were quite satisfactory in nearly every case, but that those for zinc were inaccurate, especially when the amount of zinc was small.

Third Method.—Solutions containing known amounts of gallium, indium, and zinc were diluted to about 200 cc., and 2 cc. of sulphuric acid (sp. gr. 1.84) was added to each solution. Zinc was precipitated as zinc mercuric thiocyanate in the usual manner. After standing for several hours this precipitate was collected on an asbestos filter in an unweighed Gooch crucible, and was washed with a solution containing 20 cc. of potassium mercuric thiocyanate reagent in 1 litre. The precipitate was then treated on the asbestos mat in the crucible alternately with a few drops of a strong solution of sodium hydroxide and a few drops of concentrated hydrochloric acid until it was dissolved. Four cc. of acid was sufficient to effect solution of the precipitate. The resulting solution was then diluted to about 200 cc., and the excess of acid was neutralised with sodium hydroxide. Two cc. of concentrated sulphuric acid and 20 cc. of the potassium mercuric thiocyanate reagent were then added. The contents of the beaker were allowed to stand for several hours, and the precipitate was collected in a weighed Gooch crucible which was then dried and weighed.

The combined filtrates from the two precipitations of zinc mercuric thiocyanate had a volume of about 500 cc. Ten cc. of hydrochloric acid was added to the solution, the mercury was precipitated by hydrogen sulphide, the mercuric sulphide was filtered off, and the filtrate was freed from hydrogen sulphide by boiling. The indium and gallium in the solution were determined by the method previously described.

TABLE XIV.—Separation of Gallium, Zinc, and Indium. Third Method.

	1.	2.	3.
Weight of Ga_2O_3 taken (grm.)..	0.0828	0.0166	0.0083
Weight of Ga_2O_3 found (grm.)..	0.0840	0.0163	0.0094
Weight of zinc taken (grm.) ..	0.0076	0.0188	0.0039
Weight of zinc found (grm.) ..	0.0077	0.0188	0.0039
Weight of In_2O_3 taken (grm.) ..	0.0064	0.0647	0.0130
Weight of In_2O_3 found (grm.) ..	0.0014	0.0502	0.0039

It will be seen that the results for zinc were very satisfactory and that those for gallium were fairly accurate. The amount of indium, however, was low in each case, and it was found that the precipitate of mercuric sulphide gave a strong spectrum of indium.

(To be continued).

WOLFRAM.—One of the noteworthy consequences of the war, according to *Metall und Erz*, is the great increase in the output of wolfram. Before the war the whole world-production did not exceed 10,000 tons annually. The present output is at least double that quantity. An approximate estimate gives—Portugal, Spain, France, and Great Britain, 2500 to 2800 tons; North America, 6000 tons; South America, 3000 to 3500 tons; India, Siam, the Malay States, and Australia, 5500 to 6000 tons; China and Japan, with Indo-China, 800 to 1200 tons. The stimulus has been high prices, so that a drop in market value would close some of the mines. Russia certainly possesses deposits of wolfram. South America, Spain, and some other countries favourable to Germany may be expected to ship to her wolfram ore at prices considerably below the present abnormally high level.—*Royal Society of Arts*.

A SPECIFIC GRAVITY APPARATUS FOR GASES.*

By EDWARD J. BRADY.

THE simplest method of determining the specific gravity of gas would be by means of a U-tube with liquid in the lower end, similar to the method used for determining the density of liquids. This method has not been used for gases, because of the extremely small differential pressure that would have to be measured to obtain accuracy. The pressure gauge in the preceding note makes the use of this method possible.

The apparatus devised consisted of a tall tube, through which the gas was passed, having its lower end connected with the precision gauge by means of a four-way cock. At the upper end there is a pilot flame, if the gases being measured are inflammable. The gases being measured passed through this vertical tube, which is opened to the air through a suitable burner at the top. A quarter turn of the cock cuts off the gas and connects this column of gas with the precision pressure gauge, which will immediately indicate a slight suction produced on the gauge, provided that the gas is lighter than the air. This cock may be turned a number of times to obtain check readings on the same sample of gas. Using the telescope and scale as described, we may graduate the scale to read in specific gravity direct. The gravity as shown by a tube of this kind would, of course, include any foreign matter, such as particles of dust or vapours. But, inasmuch as these materials assist in producing the differential pressure in the Pitot tube or the Venturi meter, they should be taken into consideration in applying the formula for these instruments.

Gases heavier than air, such as oxygen, carbon dioxide, &c., may also be measured, the deflection produced being in the opposite direction.

For more accurate work, where the absolute density of the gas is wanted, we might provide a vertical tube for air also. This air could be dried to eliminate the effect of moisture and the whole system surrounded by the constant temperature bath.

Where the density of hot gases relative to air are required, the vertical air pipe could be carried *within* the vertical gas pipe, so that the air would quickly assume the same temperature as the gas being measured. In many places a vertical tube of much greater height would be permissible. In this case the telescope and scale could be dispensed with and the differential pressure read from the Vernier direct.—*Journal of the Franklin Institute*, clxxvii., No. 4.

BOROUGH POLYTECHNIC INSTITUTE.

THE following Report was read at the Twenty-sixth Annual Distribution of Prizes and Certificates by Principal C. T. Millis, M.I.Mech.E., on Tuesday, May 27, 1919:—

The year ending July, 1918, the fourth year of the great war, was a memorable and trying one, but in spite of that the Institute kept up its many activities and did much good work, including war service. Of course in number of students, especially of men, we have suffered, but have probably been more fortunate than some other institutes. There were 2094 students and members in attendance during the year, 1550 being evening and 540 full time day students.

As regards examination successes, out of the 325 papers worked by evening students 209 qualified for passes. One Silver Medal and £1, being first prize in Millinery awarded by the City and Guilds of London Institute, was won by Lily K. Rowe, who was also awarded the Chairman's Prize of £3 for the best record during three consecutive

* Note from the Physical Laboratory of the United Gas Improvement Company, U.S.A.

years, being the first woman student to gain this prize. Four Medallions for First Aid and fourteen L.C.C. Evening Exhibitions in Science and Technology were gained. The boys of the Day School gained 43 diplomas and certificates on the results of a final examination and their three years of good work.

The Board of Education having given up its examinations, the Governors have drawn up a scheme of Institute Examinations, and students under definite conditions will be able to obtain diplomas for successes at examinations in organised courses of study extending over three years. The scheme is an important one, requiring care and thought. We believe the diplomas will be recognised outside the Institute as being of real value as evidence of sound work on the part of the students. A careful perusal of the examination lists in your hands will show that many students by their successes in two or more subjects during their first and second years are on the way towards gaining the Institute Diplomas to which I have referred, and, indeed, some students have qualified for the Diplomas. Diplomas and Certificates will be ready shortly.

I repeat what I have said on former occasions. Much work done by pupils of the Institute is not shown by examination results; for example, the Girls' Trade School at present has no certificate examination scheme. The real test of our work lies not in examination results but in the progress of our students. We have ample evidence in their successful careers that their studies have been of real value to them as citizens and workers. This has been shown during the war.

The staffing of the Institute during the past two or three years has been very difficult, and we have been fortunate in having the services of three mistresses who have done good work for our Boys' School. Much extra work and responsibility have been thrown on the permanent teaching staff and officials, who have willingly responded. I must pay a well deserved tribute to the zeal and energy of those Heads of Departments and the Staff generally who have so loyally helped me to carry on. Many appointments have now to be made to replace the temporary staff. Dr. Henderson, Head of the Electrotechnics Department, who has been on service for some time, has resigned, having been appointed Staff Officer for the Army Education Scheme.

I am sure you will all bear with regret that our Lady Superintendent is retiring in July next. Miss Smith, Mr. Richardson, and I were appointed in 1892 to start the work of the Institute (Mr. Richardson retired in 1915). Miss Smith and I have worked together for twenty-seven years, and naturally I shall miss her very much. It is not an easy matter to do justice to her work. All who have worked with her here know the splendid work she has done. She is the pioneer of the Girls' Trade School movement, and no one will be able to give more energy, thought, and devoted service to the Institute than she has given. I am sure that the staff, members, and students will desire to join with me in wishing her many years of health and happiness in her retirement.

I now pass to the consideration of the future work of the Institute. We feel that next session there will be a considerable increase in the number of students, which will tax the accommodation to its utmost. There is some doubt at present as to the effect of the new Education Act on our work in the future. Young persons of fourteen to sixteen years of age will doubtless receive education of a more or less general character and will be accommodated in special buildings. The compulsory part time education for those between sixteen and eighteen will not come into operation for seven years, and in that work this Institute may be expected to take a prominent part so far as science and technical work is concerned in both day and evening classes. Our Branch Institute, Herold's Institute, Bermondsey, will probably at first be utilised in the day time for the pupils of fourteen to sixteen years of age. One effect of the compulsory part-time day continuation education

will be an increase in the number of girls and boys seeking admission into junior technical schools, because the new Education Act grants exemption from attendance at part-time day courses to those children who have attended full-time day classes up to sixteen years of age, and this will act as an incentive to thoughtful parents to keep their children at such schools until that age. Moreover, employers will be more likely to engage workers at sixteen years of age who are exempt from attending school than to engage those at fourteen years of age who will be compelled to attend eight hours a week in the day time until they are eighteen.

Then, again, it will be necessary to consider how our evening education will be affected by this Act. If the part-time day education is properly planned and directed it should stimulate the pupils to further efforts and provide us with a large number of students able to go on with higher work than at present. The work of the Mechanical Engineering, Electrotechnics, Chemistry, and other departments of the Institute will have to be extended in the future, and probably the methods of instruction, particularly in the laboratories and workshops, may require modification to meet changing and specialised methods of production. The compulsory part-time day education will doubtless exert an influence on our evening work outside that of science and technology. Owing to the co-ordination of education in London, our work is becoming more technical, and therefore we must pay increased attention to the study of subjects of general interest, such as music, literature, modern languages, social and industrial economics, industrial history, to enable our students to broaden their training and make intelligent use of the extra leisure which we hope they will have in the future. I am aware that this is not an easy task, and I appeal to the members and students to give all the assistance they can to help in the development of this side of our work, so that the Governors may be able to provide facilities for them to become not only good workers but good citizens for this great country of ours.

Now the war is over and peace is in sight I may briefly review the war services rendered by the Institute.

We know of over 350 students and members who voluntarily joined the Army. The *Polytechnic News* has been sent each month to members on service. This was done at the suggestion of Mr. Edric Bayley, who largely defrayed the cost of postage and printing. Letters have been received from all parts of the world and published in the *News*. Service members and students have expressed their appreciation of the Institute's efforts to keep in touch with them.

I regret to say that of these over 100 have made the great sacrifice. They will not be forgotten, and their names will be recorded on the War Memorial which it is hoped to place in the Institute. Many distinctions have been gained and a number of commissions have been obtained.

Early in the war our Farriery Institute in Bermondsey proved of the greatest service to the Army in training at a critical time over 1500 men belonging to the Royal Field Artillery, the Royal Engineers, and Army Service Corps in cold shoeing. The Institute was also lent for the reception, inspection, and dispatch of horse-shoes required for the Army. I do not think the value of this work has been sufficiently appreciated.

Instruction was given in the Polytechnic at the beginning of the war in telephony, wheelwrights' work, and saddlery to 100 men of the Royal Field and Royal Horse Artillery. A member of the Chemistry staff was given a commission in the Sanitary Section, and over thirty men of the R.A.M.C. were trained in water analysis. Our Chemistry staff took an active part, with other Polytechnics, in the preparation of drugs for local anaesthetics not previously made in this country, and also rendered services in utilisation of waste products, for which letters of thanks have been received.

From July, 1915, until the Armistice was signed our

engineers' workshop with the staff was given up to munitions work, and over 10,000 inspection and other high-class gauges so necessary for munitions work were manufactured, and successfully passed the tests of the National Physical Laboratory. A really fine record of work.

The Southwark Volunteer Corps was started in the Institute, with Major Basil Williams, a member of the Governing Body, as its Commandant. The Institute gymnasium, rifle range, and the athletic ground were lent, and proved of great service to men of the New Army as well as to the volunteer corps.

The Southwark Voluntary Aid Detachment was started by our members, with Miss Swayne as Commandant, and has done excellent work in hospitals. From the commencement of air raids until the end of the war the Institute was used as a dressing station and as a refuge, members of the V.A.D. being in attendance every night, and they and the working staff deserve great praise for their devotion to duty. A presentation of watches, medals, and certificates was made by the Governors at the re-union on Empire Day.

The members, evening students, girls and boys of the day schools have collected very nearly £400 for soldiers' comforts and other funds. The girls and women students and members have also worked a large number of articles for soldiers and for the Red Cross Society.

Considerable attention has been paid to the training of disabled soldiers to enable them to become dental mechanics and motor mechanics, over 150 having been in training. Advice and assistance has also been given to help forward the Army Education Scheme, and a large number of Army and Ex-Army men have received technical training.

The large hall and men's gymnasium were lent for the manufacture and Government inspection of anti-gas masks; from 15,000 to 18,000 being sent out every day.

I think I have said enough in this brief survey to give you some idea of the service which the Institute has rendered in connection with the war, and I believe you will agree with me that it forms a record of which we have every reason to be proud.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY CONVERSAZIONE.

THE first Soirée since 1914 took place on May 28. The gathering was quite on the old lines, and many familiar faces were seen in the rooms at Burlington House. The absence too of many was noted, for during the past four years many prominent men of science have passed away.

The meeting was very well attended, and although there was nothing particularly striking in the exhibits there were many of considerable interest, showing that even during the war there has been found opportunity for research in other fields than those devoted to annihilation.

Among the more important exhibits were the following:—

Prof. ERNEST WILSON. Instruments for measuring Minute Susceptibilities, including a Portable Instrument for Survey Work.

The action of the instrument depends upon the mechanical force exerted by a magnetic field on a magnetic material placed in it, the force per unit volume being proportional to the gradient of the square of the field. It is ultimately measured by a galvanometric method involving the action of a spot of light, except in the case of the portable instrument, when a pointer is more convenient.

Prof. H. F. NEWALL, F.R.S. Dr. G. E. Hale's photographs of the Zeeman Effect in the Spectra of Sunspots.

An image of the sun's disc is thrown by means of the 150 ft. tower telescope at Mount Wilson on the slit plate

of the 75 ft. spectrograph. Close to the slit a Nicol prism is placed. Above the Nicol prism are mounted strips of mica 2 mm. wide with their axes inclined $+45^\circ$ and -45° to the length of the strips, alternating in adjacent strips. This device is called a compound quarter-wave plate.

When a sunspot near the centre of the sun's disc falls on the slit through the polariscopic apparatus, certain lines in the spectrum are widened, others are resolved into two or three components.

From a comparison of the solar effects and of the magnitude of the Zeeman effect in experiments in the laboratory on the corresponding lines, the strength of the magnetic field in the sunspot is deduced.

Average spots exhibit fields ranging from 2000 to 2700 gauss. The field varies approximately in proportion to the size of the umbra.

Mr. A. MALLOCK, F.R.S. Apparatus used in the measurement of the Growth of Trees.

An "Invar" tape was passed round the tree and over the "Rockers" on the apparatus whose arms control the angle between a plane glass surface and the face of a right-angled glass prism. The growth of the tree continually alters this angle, the variation of which was measured by observing the change of position of the interference bands formed, at grazing incidence, between the plane and prism. The details of the procedure are given in *Proc. R.S.*, 1918, xc., B., p. 186 *et seq.*

Dr. J. S. HALDANE, F.R.S. Army form of apparatus for continuous Oxygen administration.

In cases of poisoning by irritant gas, and in various other conditions, one of the main dangers is due to the fact that the partial pressure of oxygen in the lungs becomes inadequate to oxygenate the blood. It is therefore necessary to add oxygen to the inspired air until a sufficient degree of recovery takes place. With the help of a reducing valve and graduated tap, a constant stream of oxygen of the required amount is delivered into the small bag attached to the face-piece. This bag is emptied at each inspiration, none of the oxygen being wasted. The administration can thus be continued, if necessary, for several days, as the consumption of oxygen is reduced to a minimum.

THE DIRECTOR OF RESEARCH, AIR MINISTRY. Liquid Oxygen Container (50 lbs. capacity), and Liquid Oxygen Vaporiser Flask (5 litre).

These vessels comprise an inner and outer metal shell, the intervening space being evacuated. Charcoal is placed in the vacuum.

Sir WILLIAM GARFORTH. Photographs, &c., illustrating Pressure in Explosions.

1. Photograph of coal-dust flame, 170 feet long, being expelled from experimental tube, with particulars of registered velocities and pressures.

2. Photograph showing a shale-dust cloud being expelled from an experimental tube by an explosion of coal-dust, the flame of which was extinguished within the tube by its contact with incombustible dust.

3. Plan showing the destructive effects of a coal-dust explosion on mine workings, and how the explosion flame was extinguished on coming in contact with incombustible shale-dust.

Prof. MACGREGOR-MORRIS. Portable Apparatus for measuring Air Currents.

A Wheatstone bridge is made of four wires all exactly alike of a material whose resistivity varies with temperature. This bridge is heated by the passage of an electric current. Adjacent arms are so arranged as to be unequally cooled when placed in an air current. The apparatus can be carried on a bicycle, and has been used for determining the velocity of the wind about a cliff edge, and also around the gallery of a lighthouse.

Sir NAPIER SHAW, F.R.S. Illustrations of the Structure of the Atmosphere on selected occasions.

1. Records of wind, on tube-anemometers, corrected for the difference of exposure in different orientations.
2. Maps of stream-function of the air for different levels on the occasion of the destruction of a fleet of Zeppelins, October 19-20, 1917, and another similar distribution on October 13, 1918.
3. Theoretical maps of the stream-function of the free air and distribution of pressure in the case of a cyclone consisting of a simple vortex with maximum velocity 43 metres per second, enclosing a core of fluid-rotating-like-a-solid, in a uniform atmospheric current of 16 metres per second; with maps for 18 h., September 10, 1903, for comparison.

Dr. G. SIMS WOODHEAD and Dr. VARRIER JONES. Quasi-continuous temperature recording apparatus for clinical use, and specimens of records obtained.

The outfit consists of a resistance thermometer with compensating leads, a galvanometer with "bridge" and resistances, by means of which a wide range of temperature changes may be observed, and a Cambridge thread recorder, which gives a quasi-continuous (at half-minute intervals) and permanent record of the temperature of the human or animal body. This apparatus has been of use in determining the diurnal variations of temperature of normal subjects and in studying febrile conditions in disease, *i.e.*, tuberculosis. Continuous temperature records for seventy-two hours are readily obtained.

THE CAMBRIDGE SCIENTIFIC INSTRUMENT CO., LTD. Dr. G. A. Shakespear's Katharometer for Measuring the Purity of Gases.

Two small spirals of platinum wire form two arms of a Wheatstone bridge, and their resistances, depending on their temperatures, depend on the viscosities of the surrounding gases. A galvanometer connected across the bridge indicates its out of balance and is calibrated to give a direct reading of the purity of the gas, or otherwise as required. Many practical applications are possible: (a) A Hydrogen purity meter for use with aircraft is exhibited; (b) Permeameters for testing airship fabrics and exploring seams or searching for leaks are exhibited; (c) a humidity recorder showing the vapour pressure in the air of the exhibition room was shown working.

Mr. F. W. ASTON. Rapidly moving Striated Discharge in Neon and Helium.

The light in the capillary of a spectrum discharge tube containing neon or helium is apparently continuous, but when analysed by a rotating mirror is found to consist of a procession of alternate bright and dark bands or striations travelling in the direction of the current, *i.e.*, from anode to cathode. These appear in the mirror as ribbons of light, their waviness indicating variations in speed and being more marked in neon than in helium. The mean velocity can be calculated from the slope, and is found to be approximately that of pressure wave propagation, *i.e.*, sound, in the gas in the discharge tube.

Mr. C. T. R. WILSON, F.R.S. 1. Stereoscopic Photographs of the Tracks of Ionising Particles through Air.

By causing water to condense upon the ions set free, the invisible trail of ions left by each flying particle along its course is converted into a sharp defined line of cloud. Stereoscopic photographs of the tracks thus rendered visible are taken before convection currents have had time to distort them.

The photographs exhibited illustrate the nature of ionisation by the alpha and beta rays from radium and by X-rays.

2. Photographic record of the changes in the Electric Potential Gradient during a Thunderstorm.

The record was obtained at the Solar Physics Observatory, Cambridge, on June 13, 1917. It shows the sudden changes produced in the electric field by the passage of lightning discharges.

Mr. A. CHASTON CHAPMAN. "Mineral Yeast."—Used in Germany during the War for Human Food.

The organism exhibited is very similar to, if not identical with, the so-called "Mineral Yeast" which was manufactured in Germany in considerable quantities during the War and used to supplement the bread ration. The organism is not a true yeast—that is to say, it does not belong to the genus *Saccharomyces*. It grows freely upon nutrient solutions at a temperature of 38° to 40° C., forming a thick greasy crinkled film. It does not produce alcohol, and the time needed for a full crop is about thirty-six to forty-eight hours. The separated organism contains 50 to 55 per cent of protein (NX 6.25) and about 5 per cent of fat, expressed on the moisture-free material. It is entirely free from bitterness, and has a pleasant flavour, suggestive of that of cream cheese. As a source of carbon, glucose or molasses answer well, and the organism is capable of supplying the whole of its nitrogen needs from ammonium salts—that is to say, it does not require any organic nitrogen. In addition to the above, phosphates must be present and small quantities of potassium and magnesium salts. The conversion products of sawdust forms a good pabulum for the organism, and can be used to replace glucose and molasses.

Mr. GEORGE H. GABB. Portrait of Dr. John Jeffries, in pastel, by John Russel, R.A. Dr. Jeffries was, with Blanchard, the first to cross the Channel in a Balloon, on January 7, 1785.

The account of this epoch-making "aerial voyage" was read before the Royal Society in January, 1786. This portrait was exhibited in the Royal Academy in 1786, and was lost for over 100 years until it was discovered a short time ago, quite unknown, among a miscellaneous collection of pictures. Dr. Jeffries, although famous as being the first aeronaut to cross the Channel, his title to a niche in the Temple of Science is perhaps yet more secure to immortality as being indisputably the first to make an ascent solely for scientific purposes, and the first to attempt meteorological observations from a balloon. In his ascent from London on November 30, 1784, he included in his scientific equipment a barometer, a thermometer, a hygrometer, an electrometer, a marine compass, a telescope, and six small phials filled with water given him by Cavendish in order to collect samples of air at different altitudes. This last experiment was made at the suggestion of Dr. Blagden, Secretary to the Royal Society.

Sir ROBERT HADFIELD, F.R.S. Stereoscopic Radiographs of large Carbon Electrodes.

These electrodes are used in electric steel smelting furnaces, the largest type being no less than 22 inches in diameter. For effective and economical working of the furnaces it is essential that the electrodes do not break and fall into the bath. The finer the structure of the electrode and the fewer the inclusions, the less does the possibility of breakage arise. The stereoscope shows four different types of electrodes which are largely used.

War Research on Nitrogen Fixation.

For the past three years the Research Laboratory of the Munitions Inventions Department, constituted under the auspices of the Nitrogen Products Committee of the Ministry of Munitions, has been conducting experimental investigations on various methods for the fixation of nitrogen. The most important divisions of the work have been concerned with the Synthesis of Ammonia, the Oxidation of Ammonia and Preparation of Nitrates, and the Preparation and Purification of Hydrogen. Experiments illustrative of the work of three of the sections were shown as follows:—

1. Synthetic Ammonia Section.—Apparatus for the study of Catalysts.

An example of the small apparatus used in the study of the effect of velocity, temperature, pressure, purity of gases, &c., on the behaviour of catalysts at pressures up to 200 atm. is shown at work. In order to be able to carry out rapid tests of catalytic efficiency the dimensions are intentionally made small. Specimens representative of

several hundred preparations of catalytic materials are shown.

2. Nitrates Section.—A new process for the direct production of Solid Ammonium Nitrate.

The process depends upon the interaction of ammonia with air taking place in three stages:—

(a) The oxidation of ammonia by atmospheric oxygen to nitric oxide;

(b) The further oxidation of nitric oxide;

(c) The direct formation of ammonium nitrate from ammonia, water vapour, and oxides of nitrogen.

It had long been considered impossible to prepare ammonium nitrate free from nitrite by direct synthesis. When the different constituents are mixed in anything like molecular proportions very poor yields containing much nitrite are obtained. The results of the investigation have shown that by proper control of the experimental conditions a solid dry product free from nitrite can be obtained by a comparatively simple process. This form of ammonium nitrate differs from the ordinary crystalline material and possesses a number of interesting properties.

3. Hydrogen Section.

Seeing that three-quarters of the cost of synthetic ammonia consists in the preparation and purification of the high grade hydrogen required, a very important branch of the work has been the study of modern catalytic methods for its production at a low cost and a thorough investigation of the different methods for its purification. New catalytic processes dependent on fractional combustion have been devised and some of these have proved successful on an industrial scale. Two new developments are shown in operation:—

(i.) A recorder for indicating automatically the percentage of carbon monoxide in a flow of hydrogen.

(ii.) A process for the removal of H_2S as sulphur by fractional catalytic combustion.

Charts, diagrams, and apparatus illustrative of the Laboratory work were also exhibited.

Demonstrations were given by Major G. W. C. Kaye on the Detection of Defects in Aeroplane Timber, and by Dr. R. T. Leiper on Biological Factors in the Spread and Control of Bilharziasis.

SOCIETY OF GLASS TECHNOLOGY.

THE May meeting was held on Wednesday, the 21st ult., in the Institute of Chemistry, Russell Square, London.

Dr. M. W. TRAVERS, F.R.S., presided over a well-attended meeting.

After the usual formal business had been transacted, Dr. WALTER ROSENHAIN, F.R.S., gave a most interesting and instructive lecture on "Some Phenomena of Pot Attack." The lecture was an account of work on entirely new lines, carried out under Dr. Rosenhain's supervision by Mr. E. A. Coad-Pryor, B.A., Mr. V. Stott, M.Sc., and Miss A. B. Taylor.

In the first place the lecturer stated that research was begun on the improvement of methods for the production of optical glass. The first step was to find a material to arrest the attack of molten glass, and to endeavour if possible to discover a container entirely insoluble in glass at high temperatures. A study of glass attack upon clay was begun, and the process by which glass attacks clay investigated. These processes, owing to the novel methods used, could be carefully controlled under standardised conditions. Small pots made of china clay cast by a special method was used in the research. The furnace used was an electrical one, so constructed that temperature and atmosphere could be kept constant. The pot attack of several glasses known to be very violent in their action upon clay was studied. The amount of pot attack was measured exactly under various time and temperature conditions. The result showed that the attack was mainly on the bottom of the pot, and that holes were drilled in a

rough circular form. In many cases it was shown that the amount of attack was proportional to the depth of the clay beneath the glass surface. The explanation of the results was somewhat difficult to find, but a study of solution of solids in liquids less viscous than glass led to the conclusion that the phenomenon was due to currents set up in the liquid due to density changes. By means of a lantern the lecturer showed the processes of solution actually taking place. One of the portions of the research had been the microscopic examination of the glass and pot after attack. Much interesting information had been obtained, and slides were shown illustrating some of the results. This portion of the work is necessarily still in progress. It had been proved conclusively that holes could be drilled in a pot without having actual defects in the pot to start with. Another very interesting feature recently developed was the application of X-rays to the examination of small pots. In concluding his lecture, Dr. Rosenhain pointed out the fundamental importance of being able to do quantitative work upon the actual melting processes of glass.

In the discussion that followed, Dr. Travers, F.R.S., Mr. C. J. Peddle, M.Sc., F.I.C., Mr. E. A. Coad-Pryor, B.A., Mr. Duncan Webb, jun., and Mr. Arnold Stevenson, B.A., M.B.E., took part.

During the morning the Society paid a visit to the National Physical Laboratory at the invitation of the Director, Sir Richard Glazebrook, F.R.S., and a most interesting morning was spent in inspecting the following departments:—Engineering and Aerodynamics, Electrotechnics, Optics, Metrology, Tank, Metallurgy and Glass Research.

The best thanks of the Society are due to Sir Richard Glazebrook and Dr. Rosenhain for their splendid reception, and also to the staff of the National Physical Laboratory, who contributed so much to the pleasure of the visitors.

The next meeting of the Society will be held at Sheffield on June 18.

NOTES.

THE demand for radium for both therapeutic and physical work is steadily increasing; there is now no doubt about its value in the treatment of rodent ulcer and many forms of skin diseases. During the war it has been extensively employed for the preparation of luminous paints for the dials of instruments used in night operations on land, in the sea, and in the air; all these applications are likely to be permanent. Although the actual amount of radium in luminous paint is small—about 0.25 mgrm. of radium element to the grm. of zinc sulphide—the high price of radium compounds makes this a matter of serious consideration. A radio element having similar properties, i.e., mesothorium, is comparatively plentiful, being obtained almost as a by-product in the preparation of thorium, used in the "mantle" industry. This is now rapidly coming into use; it, however, has the defect that its "life" (the period in which its initial activity is reduced to half value) is only from five to six years, as compared with 1600 years for pure radium. At the present moment there appears to be no ready way of distinguishing the one compound from the other. In a great many of its applications a life of six years is quite sufficient, but, on the other hand, where it is used for medical and some other purposes, the matter becomes very serious. It is to be hoped that some means may be found for clearly distinguishing between the two compounds.

FARMERS AND FERTILISERS.—At the close of the present month the control exercised for the last two years by the Board of Agriculture over the prices of fertilisers to farmers comes to an end. What that control has meant to farmers in the supplying of fertilisers at considerably

less than prime cost may be gathered from a statement by Lord Ernle, President of the Board of Agriculture, in the House of Lords on Wednesday, May 7, when he stated that "the assistance given to the farmer with his fertilisers has cost the State something like £1,600,000 last year." The manufacture of superphosphate and compound manures (only one section of the fertilisers referred to by Lord Ernle) has been controlled during these last two years by the Ministry of Munitions, which supplied the manufacturers with the raw materials on a basis which permitted the sale of superphosphate and compound manures at the price fixed by the Food Production Section of the Board of Agriculture, these being such as to encourage a liberal use of artificial manures by farmers in the interests of the maximum possible food production within these Islands. Now that the control of the fertiliser industry, with others, is being abandoned and the manufacturers have to supply themselves with their raw material at the market prices and independently of Government aid, it must naturally follow that the prices of manufactured fertilisers must be based upon the cost of raw materials. The farmers of the country must, therefore, anticipate after the close of the present month a substantial increase in the price of superphosphate and compound manures, which will continue until such time as the present high overseas freights return to a more or less normal level.

CAUTION AS TO WORTHLESS MANURES.—A correspondent has forwarded a circular sent out by a certain firm—not one of the recognised manure manufacturers—offering as fertiliser a material described as a complete mineral plant food at the price of £10 per ton. Analysis showed that the material contained no nitrogen, no phosphate, and only a small amount of potash; there was, however, a little calcium carbonate, but the bulk was inert mineral matter. Farmers and allotment holders cannot be cautioned too strongly against specious advertisements claiming unusual powers for particular proprietary articles. A large number of experiments have been made by fully qualified and disinterested persons in many parts of the country and with many crops and substances, and no authentic record exists to show that any substances are of use as fertiliser to farmers in this country except compounds of nitrogen, phosphorus, potassium, certain compounds of calcium (*i.e.*, lime, limestone, and gypsum), and sodium (salt and sodium sulphate). Most of these substances are worth buying. A few experiments indicate that magnesium compounds may, under certain circumstances, be of some use, though not very much; in Italy manganese compounds have been supposed to be of value, though British experiments have not supported this view; while iron compounds have also been considered as fertilisers. Neither magnesium, iron, nor manganese compounds, however, are worth paying for, as their action is far too uncertain to justify expenditure by any except the most adventurous of experimentally-minded growers. As to other substances there is still less indication that they ever possess value. Before paying for any fertiliser farmers should demand the proper invoice and should see that they are really obtaining full value for their money.—*Journal of the Board of Agriculture*, May, 1919.

THE Federation of British Industries are organising a British Manufacturers Exhibition in Athens, to be held in October and November next, and at the present moment there is a great demand in Greece for practically every description of manufactured article produced in this country. The fact will probably be appreciated that the Exhibition affords an exceptional opportunity of introducing goods to Greek buyers in advance of manufacturers of other nationalities. There is still some space available in the Exhibition, but early application is advisable from manufacturers. The articles mentioned by the Federation's Special Commissioner in Athens as being greatly in demand are as follows:—Machinery of every description, particularly agricultural machinery; Railway rolling

stock, &c.; Cotton goods and clothing of every description; Boots and shoes; Electric dynamos, &c.; Automatic telephones; Fertilisers and chemicals generally; Food products; Toilet requisites, soaps, &c.; Household requisites of every description; Jewellery; Stationery; Furniture (both Household and Office); &c.

BRITISH CHEMICAL STANDARDS (CHROME-VANADIUM STEEL "V").—In response to a special appeal to prepare alloy steel standard turnings of the above type, a supply has been obtained and analysed by three Government Departments, a number of independent analysts, steel manufacturers, and motor or aero makers' chemists, thus representing in the main the different sections of the industries concerned. The analysis is as follows:—

Carbon	0.574 per cent
Silicon	0.158 "
Sulphur	0.063 "
Phosphorus	0.024 "
Manganese	0.543 "
Arsenic	0.015 "
CHROMIUM	0.858 "
VANADIUM	0.271 "

The turnings are now available at a price just sufficient to cover the cost and are packed in 50 and 100 grm. lots, with each of which is issued the usual certificate giving details of the analysis. Further particulars may be obtained from Headquarters, 3, Wilson Street, Middlesbrough.

ATTENTION is directed to the new Government publication *Surplus*, the official organ of the Surplus Government Property Disposal Board, Ministry of Munitions, which will be published on the 1st and 15th of every month. The first number just issued is a thoroughly businesslike production. It enumerates the great variety of surplus war material that is for disposal all over the country, and is so classified that manufacturers and traders are able to get in touch at once with the materials they wish to secure. A long list of chemicals for disposal is given, in quantities varying from a few pounds to tons. Among the "miscellaneous stores" the following chemical apparatus appears:—Fortins Barometer (in case). Chemical Balances Oertling, Nos. 21, 32a, 7.S.B., 8.S.B.2. Platinum crucibles, foil, basins, and rods. Thermometers, Gas Meters. Iron stands for Lunges. Gas volumeters. Hydrometers, Geryk Vacuum Pump Duplex C. Electric Motors, 110 V.A.C. Clamps, Fletcher's Aspirators, Gutta Percha Nitrometer, also a large quantity of glass and other Laboratory fittings. (Lying at Oldbury. Reference D.B.5.C.). Also Large Glass Aspirators, Amp and Volt Meter and Resistance coil. Calorimeter by Alex. Wright—for fuel testing with thermometer, Electric control, Ether thalpelassimeter Steam oven, fitted with still. Portable pyrometer (by Scientific Co., Cambridge), High temperature (boiler) Thermometers, 4 and 5 ft. steel sheaths. Wash bottle, capacity 1 litre. Water purification apparatus (incomplete). A large quantity of Hydrometers, also glass and other laboratory appliances. (Lying at Victoria Works, Northwich. Reference D.B.5.C., Caxton House, Westminster, S.W. 1.) Applications for copies of *Surplus* are being received in large numbers by the Ministry, but it should be known that orders for its delivery can be placed with newsagents. The price is 3d. for each number.

MEETINGS FOR THE WEEK

Monday, June 16.

Royal Geographical, 8.30. "Tibesti to Darfur," by Lieut. Col. J. Tilho.

Thursday, June 19.

Institution of Mining Engineers, 11 a.m. (Dinner at Waldorf Hotel, 7).

Friday, June 20.]

Institution of Mining Engineers. (Visit to Docks and Warehouses of Port of London Authority).

THE CHEMICAL NEWS

VOL. CXVIII., No. 3088.

A SYSTEM OF STRUCTURE SYMBOLS.

By INGO W. D. HACKH.

THE idea underlying a system of structure symbols for organic compounds was first published about a year ago (*Canadian Chem. Journ.*, 1918, ii., 135). Although the principle remained unaltered its form has passed since that time through various stages of development (*Science*, N.S., 1918, xlviii., 333), making it possible to present it now in a more perfected form.

The system is based upon an extremely simple principle which does not involve any new conception but merely provides an efficient, compact, and accurate device for the representation of certain facts of organic chemistry. It is well known that certain information regarding organic

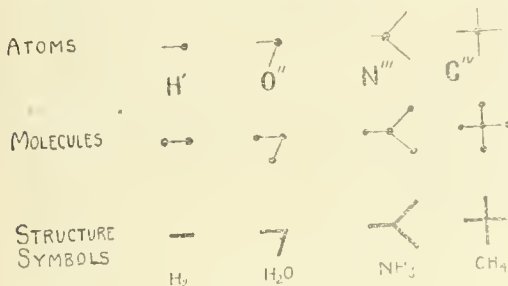


FIG. 1.

compounds is conveyed in a progressive series of (a) empirical, (b) rational, and (c) structural formula, the last type being the most advanced form. Unfortunately the space occupied by structural formulæ restrict their use mainly to didactic purposes in the illustration of isomerism and stereo-isomerism. The system of structure symbols enable a more extensive use of the information contained in structure formula, at the same time preserving clearness and accuracy and limiting the space, thus the ambiguity inherent to the rational formula is avoided.

Assuming a definite valency of H = 1, O = 2, N = 3 or 5, and C = 4 as being the normal condition of these four



FIG. 2.

elements in organic compounds, Fig. 1 shows the key to the system.

In this figure the atoms are represented by points from which one, two, three, or four lines respectively radiate. In the molecule these lines representing the bonds are connected, and in the structure symbols the points standing for the four types of atoms are determined by the lines thus—

- Where one line begins or ends—HYDROGEN,
- Where two lines radiate (angle)—OXYGEN,
- Where three (or five) lines radiate—NITRILE,
- Where four lines radiate (two lines cross)—CARBON.

Thus the simplest structure symbols are the ones shown for hydrogen gas, water, ammonia, and methane.

In order to avoid confusion in the structure symbols of the more complex compounds it is well to become familiar with the appearance of the different radicals and groups. Thus the symbols for the six important types of organic compounds show in each case a distinct and characteristic form. This Fig. 2 illustrates also the relationship between alcohols and ethers (methyl-ethers), aldehydes and

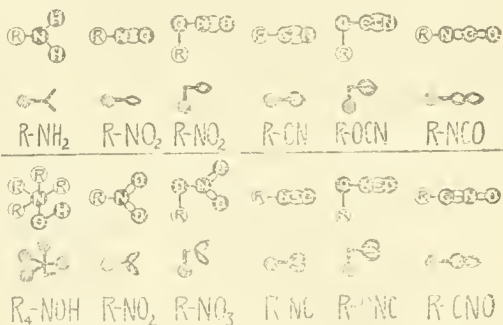


FIG. 3.

ketones, acids and esters, in each case the H being replaced by the CH₃ group. The H which is being replaced by the organic radical R is indicated in the symbols by a shaded circle. Fig. 3 gives the symbols for a number of organic nitrogen compounds, illustrating schematically the relationship of tri- and penta valent N.

With the help of the above principle the structure symbols of Figs. 4 and 5 will be readily deciphered. In

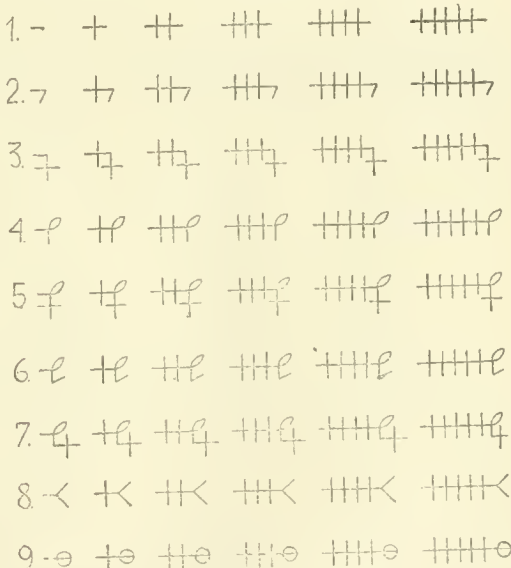


FIG. 4.

the first row are the hydrocarbons, row 2 shows the alcohols, row 3 the methyl-ethers, row 4 the aldehydes, row 5 the methyl ketones, row 6 the acids, row 7 the methyl esters, row 8 the mono-amines, row 9 the cyanides. It is interesting to note that in this systematic schema CH₃OH and CH₃COH is listed twice, namely as alcohol and aldehyde, and also as "hydrogen-methyl-ether" and "hydrogen-methyl-ketone." The benzene derivatives and the illustration of the ortho-, meta-, and para-compounds need no comment.

In the practical experience gained in teaching organic chemistry by this method it has become advisable to formulate a few rules—

Aliphatic chains containing more than six carbon atoms

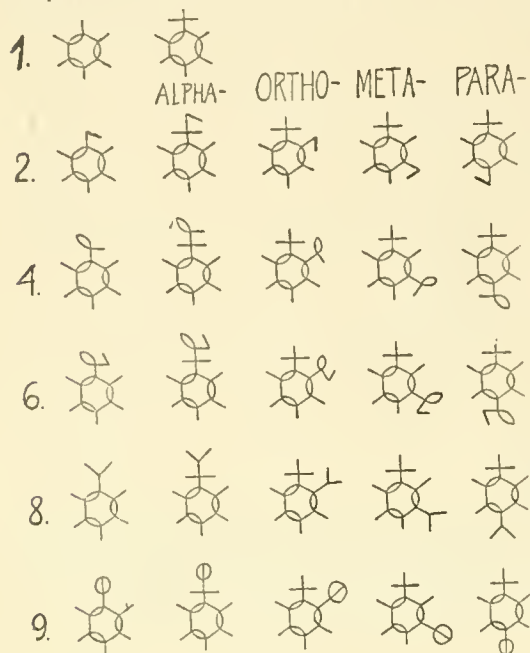


FIG. 5.

are written alternately short and long, the fifth line being longer in order to enable an easier count.

Asymmetric carbon atoms are indicated by a dot (Fig. 6)

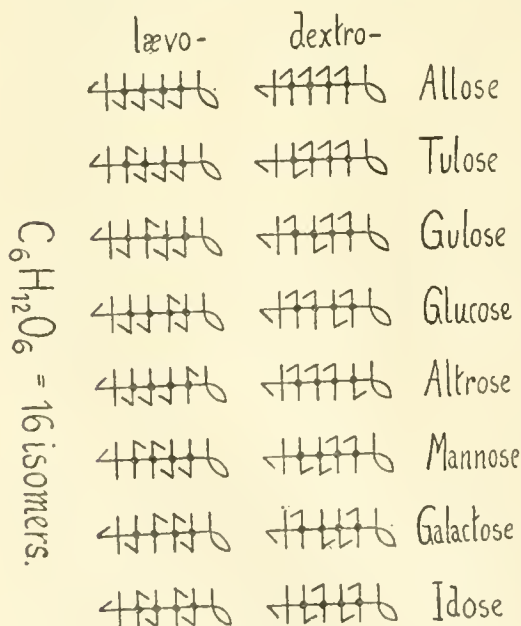


FIG. 6.

at the junction of the two lines; the rotatory power of the compound is indicated by the direction of the tail of the

—C—OH group; in levo-compounds this points in the direction of the clock-hand movement, in dextro-compounds in the reverse direction, in inactive compounds the direction of the different tails will balance each other, in racemic compounds the dot indicating asymmetric carbon atoms is eliminated.

All other elements entering into an organic compound are represented by their respective "inorganic" symbol, e.g., Cl, I, Br, S, Fe, &c.

Heterocyclic rings are better characterised by indicating the heterocyclic atom (N or O) by a dot outside the ring. The nitrogen-hydrogen line is preferably written toward the centre of the ring, thus attention is drawn to the point of interest.

In Fig. 6 the sixteen isomeric hexoses are given, and it is noteworthy that the information contained in such a narrow compass would have required at least a full printed page if the customary writing of structure formulae had been employed.

As has been pointed out in the preliminary papers the advantages of the system are numerous, for they save space and time and are valuable in the class-room. Their simple principle is without exception readily understood by the student and force him to write a theoretically correct structure, otherwise not all the given atoms would be represented. This leads to accuracy and a definite placing of eventual double or triple bonds. The accuracy and compactness of the symbols should make them also of value in abstracting and in hand-books where ordinarily the structure formula of an organic compound is omitted. The writer hopes that the system may become of service to the chemical world and will be glad to accept constructive criticism.

College of Physicians and Surgeons,
San Francisco, April 19, 1919.

GALLIUM.*

By L. M. DENNIS and J. ALLINGTON BRIDGMAN.

(Continued from p. 283).

The Separation and Determination of Gallium, Indium, Zinc, and Aluminium.—Solutions that contained known amounts of gallium, indium, zinc, and aluminium were treated essentially as previously outlined, up to the first precipitation of gallium by sodium sulphite. In this precipitation the hydroxides of both gallium and aluminium were precipitated by sodium sulphite, and this mixture of hydroxides was then dissolved in hydrochloric acid, and the gallium and aluminium were then separated by the method described previously.

TABLE XV.—*The Separation of Gallium, Zinc, Indium, and Aluminium.*

	1.	2.	3.
Weight of Ga_2O_3 taken (grm.)..	0.0828	0.1056	0.0414
Weight of G_2O_3 found (grm.)..	0.0797	0.1052	0.0429
Weight of In_2O_3 taken (grm.) ..	0.0323	0.0323	0.0647
Weight of In_2O_3 found (grm.) ..	0.0320	0.0328	0.0655
Weight of zinc taken (grm.) ..	0.0376	0.0376	0.0939
Weight of zinc found (grm.) ..	0.0363	0.0381	0.0939
Weight of Al_2O_3 taken (grm.) ..	0.0841	0.0841	0.0280
Weight of Al_2O_3 found (grm.) ..	0.0852	0.0840	0.0273

The results given in Table XV. show that the determination of each of the four elements was fairly satisfactory in all of the three analyses.

These preliminary experiments upon the analytical

* This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by J. Allington Bridgman in partial fulfilment of the requirements for the degree of Doctor of Philosophy. From the *Journal of the American Chemical Society*, 41, No. 10.

separation of gallium, indium, zinc, and aluminium indicated that the most accurate results would be obtained by the determination of zinc and gallium in one sample and of indium and gallium in a second sample, the aluminium being determined in either of the two samples.

Further investigation in this direction led to the adoption of the procedure described below.

Method of Analysis of Mixtures containing Gallium, Indium, Zinc, and Aluminium.

Neutral or slightly acid solutions of two samples of the material to be analysed are prepared. Sample 1, in which zinc and gallium (and aluminium) are to be determined, should not contain more than 0.1 grm. of zinc. Sample 2, in which indium and gallium (and aluminium) are to be determined, should not contain more than 0.1 grm. of indium. The accurate determination of zinc is made in Sample 1; that of indium in Sample 2. Gallium and aluminium may be determined in whichever of the two samples these elements are present in amounts most suitable for analysis.

Determination of Zinc and Gallium (and Aluminium) in Sample 1.—The neutral or slightly acid solution of the sample is diluted to 200 cc. and 2 cc. of concentrated sulphuric acid is added. The reagent solution of potassium mercuric thiocyanate (see *ante*) is then added drop by drop to the solution, which is vigorously stirred throughout the addition. After the precipitate has begun to form 20 cc. more of the precipitant is added, and the solution is allowed to stand for several hours with occasional stirring. The precipitate is then collected in an unweighed Gooch crucible, and is washed with a solution that is prepared by diluting 20 cc. of potassium mercuric thiocyanate reagent to 1 litre. A few drops of a concentrated solution of sodium hydroxide and then a few drops of concentrated hydrochloric acid are alternately poured upon the precipitate, and between successive additions of these reagents small quantities of water are run through the crucible. The precipitate should be entirely dissolved by the use of not more than 4 cc. of hydrochloric acid. If this solution of the zinc precipitate is acid it is neutralised with sodium hydroxide; if it is alkaline it is neutralised with sulphuric acid. It is then diluted to 200 cc., 2 cc. of concentrated sulphuric acid is added, and the zinc is precipitated with 20 cc. of the potassium mercuric thiocyanate reagent in the manner above described. After several hours' standing the precipitate is filtered through a weighed Gooch crucible, and is washed with the dilute solution of potassium mercuric thiocyanate above mentioned. The precipitate is then dried in the crucible at 105–110° and is weighed. The zinc factor is 0.1314.

If it is desired to determine gallium, or gallium and aluminium, in this sample the filtrates from the two precipitations of zinc are combined, 5 cc. of concentrated hydrochloric acid is added to the solution, and the mercury is precipitated by hydrogen sulphide. The precipitate of mercuric sulphide is filtered off and washed. The filtrate is boiled to expel hydrogen sulphide and is then neutralised with sodium hydroxide. 1.5 grms. of sodium hydroxide dissolved in a little water is then added to the solution, which is next boiled for several minutes. The resulting indium hydroxide is collected on a filter-paper and is washed with hot water, and the filtrate is set aside. The precipitate of indium hydroxide is then redissolved in hydrochloric acid, the solution is diluted to 100 cc., 1.5 grms. of sodium hydroxide is added, and the solution is again boiled to reprecipitate indium as the hydroxide. This precipitate is collected on a filter and is washed with hot water; the filtrate from this precipitation is then combined with the filtrate from the first precipitation. 1.5 grms. of hydrated sodium sulphite, $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$, is dissolved in a little water and is added to the solution. Hydrochloric acid is next run in, a drop at a time, until the solution is distinctly acid to litmus paper. The liquid is then boiled for about six minutes. The resulting precipitate consists of gallium hydroxide together with

aluminium hydroxide if aluminium is also present. It is collected on a filter-paper and is washed with a little hot water. To make sure that the precipitation of gallium has been complete a small amount of sodium sulphite is added to the filtrate and the solution is boiled for several minutes. If no precipitate results the solution is made slightly acid with acetic acid and is boiled for a further twenty minutes. Any additional precipitate from either of these treatments is added to the precipitated hydroxide first obtained.

If no aluminium is present the gallium hydroxide is dissolved in hydrochloric acid and the solution is diluted to 200 cc. The solution is then made slightly alkaline with ammonium hydroxide, and 1.5 grms. of hydrated sodium sulphite is then added. The solution is then made slightly acid with hydrochloric acid and is boiled for about six minutes. The resulting precipitate of gallium hydroxide is collected on an ashless filter-paper and is washed with water until free from chlorides. The filtrate should be tested as above described to ascertain whether the precipitation of gallium has been complete. The gallium hydroxide is dried on the paper and is incinerated over the Bunsen flame and weighed as Ga_2O_3 .

If aluminium is present the precipitate of the hydroxides of gallium and aluminium is dissolved in not more than 25 cc. of concentrated hydrochloric acid. An equal volume of ether is added to this solution. The flask is immersed in cold water and the solution is saturated with hydrogen chloride. The precipitated hydrated aluminium chloride is collected on an unweighed Gooch filter. The precipitate is washed with a small amount of a cold mixture of equal volumes of concentrated hydrochloric acid and ether, this mixture having first been saturated with hydrogen chloride. The precipitate is then dissolved in water, and the aluminium is determined by precipitation with ammonium hydroxide in the usual manner. The filtrate from the aluminium chloride precipitate contains the gallium. One cc. of sulphuric acid is added to this solution, which is then boiled until most of the ether and hydrochloric acid have been expelled. The solution is then diluted to 200 cc., and the gallium is determined by precipitation with sodium sulphite in the manner above described.

Determination of Indium and Gallium (and Aluminium) in Sample 2.—Sample 2, in which indium is to be determined, is diluted to 100 cc., and 1.5 grms. of sodium hydroxide in excess of the amount of this substance required to neutralise the solution is added. The liquid is then boiled for several minutes, and the resulting precipitate of indium hydroxide is collected on a filter-paper, is washed with hot water, and is then dissolved in hydrochloric acid. This solution is neutralised with sodium hydroxide as before, 1.5 grms. of sodium hydroxide is then added, and the solution is boiled for several minutes. This second precipitate of indium hydroxide is dissolved in hydrochloric acid, ammonium hydroxide is added until the solution is slightly alkaline, and the liquid is boiled for several minutes. The precipitated indium hydroxide is collected on an ashless filter-paper, is washed with hot water, and is then dried. It is next ignited in a weighed crucible over a Bunsen flame, the crucible is allowed to cool, the oxide is moistened with a few drops of nitric acid, is heated carefully to remove the excess of nitric acid, and is then again highly heated over a Bunsen flame and is weighed as In_2O_3 .

The alkaline filtrates from the two precipitations of indium by sodium hydroxide contain the gallium and aluminium that may have been present in the sample. To determine these two elements the solution is neutralised with sulphuric acid, and then 1 cc. of concentrated sulphuric acid is added for every 100 cc. of the solution. Zinc is precipitated from this acid solution by the addition of from 30 to 40 cc. of the potassium mercuric thiocyanate reagent. The contents of the beaker are allowed to stand for several hours, and the precipitate is then collected on a filter and is washed with a solution containing 20 cc

of the potassium mercuric thiocyanate reagent to the lute. Five cc. of hyd. ozonic acid is added to the filtrate, and mercury is then precipitated by hydrogen sulphide, the mercuric sulphide is removed by filtration and is washed, and the filtrate is then freed from hydrogen sulphide by boiling. Gallium and aluminium may then be determined in this solution by the method described under "Sample 1."

The oxides of gallium, indium, and aluminium are somewhat hygroscopic. For this reason the crucible that contains the ignited oxide should in each case be weighed in a stoppered weighing bottle.

Results that were obtained in analyses of mixtures containing gallium, indium, zinc, and aluminium by the use of the methods just described are given in Tables XVI. and XVII.

TABLE XVI.—Determination of Zinc and Gallium in Sample 1.

	1.	2.	3.
Zinc taken (grm.)	0.0076	0.0188	0.0939
Zinc found (grm.)	0.0077	0.0188	0.0939
Ga ₂ O ₃ taken (grm.)	0.00828	0.0166	0.0083
Ga ₂ O ₃ found (grm.)	0.00840	0.0163	0.0094
Ind ₂ O ₃ present (grm.)	0.0064	0.0067	0.0130

TABLE XVII.—Determination of Indium, Gallium (and Aluminium) in Sample 2.

No.	Ind ₂ O ₃ taken. Grm.	Ind ₂ O ₃ found. Grm.	Ga ₂ O ₃ taken. Grm.	Ga ₂ O ₃ found. Grm.	Al ₂ O ₃ taken. Grm.	Al ₂ O ₃ found. Grm.	Zinc present. Grm.
1.	0.0323	0.0328	0.1056	0.1052	0.0841	0.0840	0.0376
2.	0.0647	0.0655	0.0414	0.0429	0.0280	0.0273	0.0939
3.	0.0323	0.0320	0.0828	0.0797	0.0841	0.0852	0.0376
4.	0.0130	0.0129	0.0828	0.0813	None	—	0.0188
5.	0.0323	0.0318	0.0828	0.0827	None	—	0.0367
6.	0.0647	0.0650	0.0828	0.0821	None	—	0.0939
7.	0.0065	0.0063	0.0828	0.0817	None	—	0.0075
8.	0.0323	0.0335	0.0083	0.0079	None	—	0.0939
9.	0.0194	0.0195	0.0083	0.0061	None	—	0.0939
10.	0.0647	0.0650	0.0083	0.0085	None	—	0.0075

(To be continued).

THE NATURE OF THE LIQUID SURFACE.*

By H. R. PROCTOR, D.Sc.

Most scientific people have noticed the curious persistence of errors which, once they have crept into text-books, are copied from one to another without question. The experienced hand notes them and passes on, being generally too busy to correct the legion of text-books even if he reads them, but to the student they are often a source of much perplexity and misunderstanding. It is this consideration which induces me to discuss a statement which has appeared in recent books on colloid chemistry, and has even formed the basis of elaborate theories of the colloid state, but which I believe to be entirely without basis in fact. It is, to quote from a recent work, "that the surface is under greater pressure than the bulk of the liquid owing to the contracting force of surface tension"—"a conclusion which has many important corollaries"—and, of course if the conclusion is unsound the corollaries fall with it. The error seems to have arisen from assuming that surface tension was the cause instead of the effect of internal pressure, and so "putting the cart before the horse."

I fear that to make the case clear to chemists who are not physicists I must deal with some rather elementary matters, for which I apologise to those to whom they are

already familiar. The internal pressure of liquids is simply the result of the mutual attraction of their molecules, which holds them together and prevents them from flying off into vapour, and is analogous to (if not identical with) the cohesion of solids. In liquids, however, the molecules, being further apart, and equally attracted from all sides, can move freely *within* the liquid surface, though to liberate them from it, the large amount of energy known as the "heat of evaporation" must be expended. It may seem curious at first sight that these attractions, enormous as they can be shown to be at molecular distances, are so little obvious to ordinary observation, but it must be realised that they are intra-molecular and confined within the liquid surface, and, that to be truly within the liquid in a molecular sense, a body must be actually dissolved in it. The attractions diminish very rapidly with distance, so that they are only really effective over spaces which must probably be measured in hundred-millionths of a mm. Thus they are generally negligible in gases unless strongly compressed, when they diminish elasticity, and even bring about liquefaction. In Van der Waals' well-known gas-equation, $(p + \frac{a}{v^2})(v - b) = RT$, the term $\frac{a}{v^2}$

represents these attractions or internal pressure, which thus behaves as a direct addition to the external pressure, while b is a correction for the actual volume of the molecules which cannot be compressed. When these corrections are taken into account with suitable constants the gas equation holds very approximately even for liquids.

So far it has proved impossible to measure the internal pressure directly, though qualitatively it can be proved to exist. It has been shown that quite large forces are required to break the continuity of a gas free liquid sealed in a glass tube so that no free surface exists, and the well known "bumping" or successive boiling of gas-free liquids is due to the difficulty of steam forming a new surface in the interior of the liquid. Indirectly, it has been shown by Stefan that in bringing a molecule into the actual surface half the work is accomplished which is required to set it free in the form of vapour, and, since the total "heat of evaporation" is known, the internal pressure overcome in bringing a molecule to the surface is easily calculated, and it proves to be enormous. For ether at its boiling-point the calculated pressure is 1284, and for water at 0°C. 11,000 atm., or about 72 tons per sq. inch.

If we imagine Stefan's molecule on the surface (that is, half in and half out) we shall see that it is attracted downwards and to all sides by the other molecules within the very small hemisphere of its molecular range of attractions, but as there are no molecules above it there is nothing to attract it upwards or counterbalance these downward attractions, while the molecules around and below it pull it at all angles of obliquity below the horizontal. By a device well known to mathematicians each of these oblique forces can be "resolved into" or represented by two smaller forces, one vertical and the other horizontal, and all these attractions of the hemisphere finally resolved into one force pulling vertically downwards, and two equal and opposed forces pulling horizontally in any two opposite directions, and these horizontal forces are what constitute surface tension, a force tending to draw together and contract the surface in every direction. On water, which has a higher tension than any other common liquid, the force amounts to about 75 dynes (say, mgrms.) across the linear centimetre.

From what has been said it will be seen that the surface tension is not a new force in itself, but merely a resolved part of the internal pressure, and in extending the surface we diminish its internal pressure to the same amount as the surface energy has been increased, or, in other words, lessen, not increase its compression. If we follow Stefan's conception so far as to suppose the surface extended to one molecule in thickness the whole of the internal pressure will have disappeared, and as there are two surfaces the whole of the work will have been done which is necessary

* From the *Journal of the Society of Leather Trades' Chemists*, iii., No. 4. (Communicated by the Author).

to convert the liquid into vapour, and there is no longer any vertical component to prevent its passing into the gaseous state.

Both the internal pressure and the surface tension diminish with the rise of temperature from the opposing effect of the heat energy. If σ_0 be the surface tension at some known temperature, and σ_t that at another, $\sigma_t = \sigma_0(1 - \gamma t)$, γ being a small constant, usually about 0.003, and the temperature being in $^{\circ}\text{C}$. Plotted on curve paper this gives a straight line, sloping down from t_0 to t if t be the higher of the two. Obviously there is a temperature at which this line must cross the zero line, and this point proves to be very approximately the "critical" temperature at which the liquid and its vapour become equal in density, and as there is no longer any distinction between them both surface and surface tension disappear. It is probable that even at ordinary temperatures the actual liquid surface, far from being a region of compression is a sort of critical layer, where a film of expanded liquid merges into one of compressed vapour, for the molecular attraction cannot cease suddenly at the liquid surface, but must attract the vapour molecules above it. This, in fact, almost follows from the theory of vapour pressure, which is the equilibrium of pressure at which as many vapour molecules fall into the liquid surface and are caught by it as escape from it in the form of vapour. Van der Waals gives a differential equation connecting the surface tension with the rate of fall of density in the surface layer. There is probably no break in the curve of density in passing through the surface, but only a very rapid change of direction. In the gas-equation the term $\frac{a}{v^3}$ expressing the internal pressure appears as a simple addition to the mechanical pressure of the gas.

Thermodynamic considerations prove that the extension of surface is accompanied by loss of heat; that is to say, that the heat energy of the liquid has been consumed in overcoming the attraction of the molecules, just as heat is consumed when a liquid evaporates. It is therefore a fair conclusion that the formation of surface is accompanied by expansion and not by contraction.

It seems a mechanical misconception to suppose that pressure applied to the surface of a liquid the particles of which are free to move in any direction could produce a local compression on the surface, since the pressure must be equally distributed throughout the liquid as if it were confined in a stretched rubber skin, to which surface tension has often been compared. Local compression could only be produced by attractive forces directed towards the region of pressure. *Ex hypothesi*, surface tension is a tension and not a pressure, and though it produces a pressure within a convex surface it must stretch and expand the surface layer itself. Such a pressure is easily observed in a drop hanging to a pipette, which recedes when the pressure is relieved by sloping the pipette, and where the radius of curvature is short, as in a very small drop, it may become very considerable. The equation to such a pressure is $p = \frac{2\sigma}{r}$ where σ is the sur-

face tension and r the radius, and the pressure increases inversely as the radius. In a globule of water in air of 0.001 mm. in radius r would be about 15 atm. Where the surface is flat no pressure is produced, and the liquid under concave surfaces is in tension, as is seen by the rise of liquids in capillary tubes.

There is one sense, however, in which the surface may be said to be under greater pressure (though not greater compression) than the bulk of the liquid. In the surface the unbalanced downward component of the attractions tends to draw a particle downward and inward with a maximum force, while within this force is balanced by others drawing in an opposite sense, so that the particle is equally free to move in every direction. A mass on the earth's surface has a maximum weight or downward pressure, but is exposed to no external pressure but that of the

atmosphere. If it were moved to the centre of the earth it would have no weight, but be exposed to the enormous compression of the superincumbent mass. Possibly the analogy is a closer one than appears at first sight; for we need not suppose that the attraction of gravitation vanishes at molecular distances, though it is probably modified by other forces, and there is some reason to believe that it varies inversely as the fourth power of the distance like that of a small magnet (Lewis, "A System of Physical Chemistry," I, p. 11, Longmans, 1916), and the differences between the attraction which governs the solar system and that which causes internal pressure may well arise from the fact that the one is exerted by enormous masses over hundreds of millions of miles, and the other by almost infinitesimal particles over hundred-millionths of a mm. The thickness of the surface film has been estimated as of the order of the last named quantity (10^{-8} cm.), and if so, two particles within it must attract each other with ten thousand million million (10^{10}) times the force they would exert on each other at 1 cm. apart, so that gravitation alone may well account for enormous attractions at molecular distances.

The facts which have been adduced are, I think, sufficient to disprove the theory of a compressed surface, but there are several other points which it is interesting to notice. I do not propose to discuss the effect of electric potential on surface tension in detail, since, important as it is to the chemist, it would open too many side issues for this paper. Since charged particles, where + or - repel others of the same sign, a charged surface tends to spread in opposition to surface tension, which, if the charge is sufficient, may even become negative. On this depends the action of the capillary electrometer which is sensitive to charges so small as 0.001 volt. The most important cases are those of charged interfaces between two liquids which are charged with opposite signs. Such charges continually arise from the accumulation of positive or negative ions on the surfaces, and probably play a leading part in the stability of emulsions and colloid solutions generally, and on their precipitation by electrolytes.

So far our attention has been practically confined to what may be called "free" liquid surfaces in contact only with their own vapour, or with an inert gas of which the influence may be generally neglected, though in some cases the gas or vapour may be so condensed on the surface by its attraction as to appreciably influence the tension. A class of surfaces, however, which are still more important in chemistry and colloid theory are those which form the interface between a liquid and a solid, or between two immiscible liquids; and here again assertions have been made and assumptions tacitly accepted which do not seem in harmony with known facts.

If one liquid be poured upon another with which it is not miscible, in a test-tube, an interface is formed between them which is much flatter than that on either of the individual liquids in air, and may be concave or convex towards the upper liquid; that is to say, the surface tension is smaller towards another liquid than to air or vapour. The cause is obvious—the whole of the attractive forces are no longer resolved on the surface as to their horizontal components, but a portion of the attractive forces of each passes through the surface and is exerted on the neighbouring liquid. It seems to be experimentally proved that, between liquids at least, the remaining common tension of the interface is equal to the difference between the two single ones if it is taken into account that in many if not in all cases some mutual solution takes place which usually lowers surface tension, and that the individual tensions to be considered are not those of the pure liquids but of the saturated solutions of either in the other. If this rule is really exact it is obviously impossible to find three liquids A, B, and C, of which the tensions $A-B+B-C$ are less than the tension $A-C$, and in no such case has ever been observed, though it has been stated that it is possible when one of the series is a solid,

and a theory of the action of protective colloids has been built on the supposition.

It appears, therefore, that with liquids at least the common tension of the interface results from the unaltered individual tensions of the two liquids acting in opposite directions, and it follows that while the positive value of the greater tension is reduced, that of the less becomes a minus quantity, and it tends, not to contract, but to spread on the surface of contact; while it is a matter of observation that many liquids, like oil on water, do not apparently spread but form lenticular drops on the surface. The explanation appears to be that when a drop of oil is placed on clean water it immediately spreads and covers the latter with a thin and invisible film, and if the surface were infinite would do so without limit. When, however, a surface becomes covered with a film of oil of a thickness approaching the range of molecular attraction its surface tension is reduced till it becomes less than that of the bil itself, which consequently ceases to spread and forms a drop. When a liquid refuses to spread on a surface of higher tension, it is because the latter is already covered with a film of grease or some other impurity which reduces its surface tension below that of the other. It has been shown that clean water will spread spontaneously on a surface of clean mercury, and of course the same reasoning applies to solid surfaces. As all surfaces attract not merely liquids but gas and vapours it is possible that in some cases the interfering film may be one of compressed gas, or of condensed vapour.

If in a system of two liquids, that with the lower tension tends to spread upon the other, this must be still more the case when of three substances the tension of one is lower than that of either of the others, since on both sides of its film the tension becomes minus, and it spreads in a thin layer between them. If the system is one of a solid (of which the surface tension, or at least the internal pressure is always high), and of an emulsion-colloid, the surface must become coated with whichever of the colloid constituents has the lowest tension, and the "adsorption" will closely obey the so-called adsorption-law, the exponent depending on the fall of attraction with the thickening of the adsorbed film (see Note). It is not improbable that such a coating may explain the action of protective colloids on suspensoid sols.

The bearing of these facts on the formation of emulsions is obvious. If two immiscible liquids are shaken together the one present in less quantity becomes mixed with the other in the form of small globules bounded by an interface of the enclosed and enclosing liquids, and whichever of the two has the highest will retain a positive surface tension, while that of the other will become negative and tend to spread, the common interface tension as a whole remaining always positive. It is obvious that the nearer the two are to equality and the less will be this common tension, and the less the tendency of the separate globules to coalesce under its influence, and if the tensions of the two became actually equal all tendency to coalesce into separate liquids would disappear, and actual solution or a permanent colloidal sol would be formed, and any slight disturbing cause, such as a difference of potential, would cause this to take place spontaneously. The more common case of permanent emulsion, however, is that in which three constituents take part. If a little soap, or alkali which forms soap with the free fatty acid be added, it lowers the surface tension of both the other constituents, and probably forms an intermediate layer between them, so that there is no longer any tendency for globules to coalesce. Many colloids when they accumulate on a surface have a tendency to undergo some condensation which is irreversible, and enables them to form an insoluble skin, and this would render the emulsion still more permanent.

It would be interesting to consider the bearing of the facts which have been stated on the Willard Gibbs theory of mechanical adsorption, which, in my opinion, has been called in to explain many actions to which it does not

apply; but any full discussion would exceed the necessary limits of this paper. The theory is based on thermodynamic considerations, and is usually stated in the form of a differential equation not very comprehensible to others than mathematicians, so that it may be worth while to explain its reasoning in other than mathematical language. If a substance of lower surface tension is dissolved in a liquid it lowers the surface tension of the latter, and Gibbs shows that such a substance tends to accumulate in the surface, and still further to lower the tension, and with it the surface energy (which is the surface tension $\times$ the surface) which tends to reduce itself in every possible way. At the same time the concentration of the substance in the surface creates an opposing osmotic pressure in the surface layer, and equilibrium is reached when the loss of surface energy is equal to the gain in osmotic. Thus, other things being equal, the more the substance reduces surface tension, and the larger its molecule (and consequently the less the osmotic pressure it exerts) and the greater will be its accumulation in the surface, and both these conditions specially apply to some of the organic substances which most lower surface tension.

The thermodynamic reasoning on which the proof depends neither attempts nor requires any explanation of the manner in which a substance lowers surface tension, or of the force which draws it to the surface; but it may be suggested that such substances are necessarily those of which the attraction for the molecules of the solvent is low, and which consequently are expelled from a region of higher to one of lower internal pressure.

It has so far proved impossible quantitatively to test Gibbs's equation, but it has been shown by Zawidzki and others (*Zeit. Phys. Chem.*, 1900, xxxv., 77) that froth contains more of the tension-lowering substance than the bulk of the liquid, and that globules of air rising through a liquid carry with them a concentrated layer in their ascent (Benson, *Am. Journ. Phys. Chem.*, 1903, vii., 532; Milner, *Phil. Mag.*, 1907, [VI.], xiii., 96).

The conclusion may therefore be regarded as proved so far as free liquid surfaces are concerned, but when we have to deal with interfaces where the tension of one of the substances is negative and the surface density is increased and not diminished, it is hard to see how the Gibbs phenomenon can occur. Nevertheless it has been freely used by advocates of adsorption theories, without a word of comment or defence, to explain adsorptions from liquids by solid bodies such as charcoal.

Note.

The adsorption formula is $\frac{x}{m} = a c \frac{1}{n}$, where x is the weight of substance adsorbed; m that of the adsorbing substance; c the volume-concentration of the solution after adsorption; a and n constants. As the adsorbing substance is porous or finely-divided, and therefore of large but indeterminate surface, x is a proportionate measure of the surface employed, and $\frac{x}{m}$ with some multiplying constant represents the weight or thickness of the adsorbed layer. a presumably represents this multiplying constant, and, theoretically, should depend on the surface of the adsorbent and not on the nature of the adsorbed body. The exponent $1/n$ represents the rate of diminution of the adsorbing attraction as the film thickens or the attraction becomes saturated. If the adsorption is a real reversible equilibrium there must for any given thickness of film be a definite solution-pressure corresponding to the concentration of the solution. This solution-pressure will increase as the film gets thicker from the lessened attraction of the adsorbent, or the greater saturation of its attraction. The formula is wholly empirical, and probably never accurately represents the actual adsorption-law, as the logs. of experimental adsorption-curves rarely if ever give exactly straight lines, but have usually a quite definite curvature.

MEASUREMENT OF THE THICKNESS OF FILM FORMED ON GLASS AND SAND.*

By EARL PETTIJOHN.

Introduction.

A LARGE amount of work has been done up to the present time on the formation of a film on the surface of glass or silica, in which water has been used as the liquid to produce the film. Thus Ihmori (*Wied. Ann.*, 1887, *xxxi.*, 1006), Parks (*Phil. Mag.*, 1903 [6], *v.*, 517), Briggs (*Journ. Phys. Chem.*, 1905, *ix.*, 617), Katz (*Proc. Acad. Wetenschappen*, 1915, *p.* 445), and Langmuir (*Journ. Am. Chem. Soc.*, 1916, *xxxviii.*, 2221) give values for the thickness of the film formed on glass, silicate, or quartz surfaces.

There is a considerable difference in the values obtained as might be expected, since the materials used differed considerably in chemical composition and nature of surface. A part of the material was in the form of small grains (sand and quartz), some being relatively coarse and some extremely fine powder. The glass used was in the form of thin sheets, in some cases curved (spherical), and in others plane. Each of these factors would have an influence on the thickness of film obtained, as would also the temperature and vapour pressure at which the film was formed. Some typical results obtained for the film thickness are given in the following table:—

TABLE I.—Film Thickness Values.

No.	Nature of material.	Film thickness.	Investigator
1.	Glass globes	0.0000033	Ihmori
2.	Cotton silicate (glass-wool)	0.0000133	Parks
3.	Sand (microscopic powder)	0.00000045	Briggs
4.	Quartz (very fine powder)	0.0000013	Katz
	Anorthite (as above)	0.0000062	Katz
5.	Glass (incandescent lamp globes)	0.00000166	Langmuir

There are two theories regarding the formation of a film on a solid. According to the first the force acting is physical in its nature, and the intensity of its effect varies inversely as some power of the distance between the two molecules concerned. The force is similar to the force of gravitation, but acts through the distance between molecules. According to this theory successive layers of molecules may be built up on the surface of a solid to a thickness such that the attractive force of the solid just equals the tendency of the outer layer of the film to evaporate.

The second theory assumes that a chemical reaction takes place and that the water taken up becomes a part of a more or less stable chemical compound. According to this theory a variable amount of water could be taken up by solids depending only on the capacity of the solid to form a loose compound with it.

The second theory has usually been assumed to hold for the film of water forming on glass surfaces, free or loosely combined alkali present in the glass, being the substance with which the water reacts. Ihmori (*loc. cit.*) found that keeping the glass in boiling water for some time decreased the amount of water which it would take up. He believed that alkali was removed during this boiling, and that the decrease in the amount of moisture taken up was due to this fact.

It seemed worth while to check the values obtained using glass and sand, having known surfaces, if possible. Since no work has been done to determine the thickest film which can form without free liquid appearing, a method of doing this was worked out. This film was compared with the film formed with other liquids to see whether there was any basis for the theory that a chemical compound formed with water.

Materials.

Solids ; Sand.—Ordinary river sand was used. It was treated with conc. hydrochloric acid until no test for iron was shown. The acid was then washed out with distilled water and the sample dried in the air. Four samples were obtained by sifting. The first sample contained all of the sand which passed the 10-mesh screen but was retained by the 20-mesh screen. The second, third, and fourth samples consisted of the fractions from the original lot retained by the 40-, 60-, and 80-mesh screens respectively. These are called 10-, 20-, 40-, and 60-mesh sands in this paper.

The grains in this lot of sand were far from spherica no two diameters being the same. An approximation of the surface was obtained by weighing a counted number of grains (4000 to 5000), to get the average weight per grain, and determining the specific gravity. On the assumption that the grains were spherical the diameter and surface of a single grain could be calculated. It was realised when these values were obtained that they were at best only approximations.

Ottawa Sand.—A single sample of sand called in this paper "Ottawa Sand," consisted of well-rounded grains. This sample gave values by the above mentioned method which were very close to the true value for the diameter and surface. It was considered to be of known surface.

Glass Pearls.—The glass pearls used were solid, round, and of various sizes, as indicated in the table below. A few, which were poorly formed, were removed from the lot by rolling them down an inclined board. Those which were not round could be easily picked out in this way. The pearls were from two different sources, and apparently of different kinds of glass. They differed considerably in specific gravity.

The first lot was purchased at retail. The material was sold under the name of "Glistening Dew" and was used to decorate fancy cards. Two samples were obtained from this lot by "elutriation." A quantity of the pearls were placed in a tube and delivered from it at a slow rate into a rising column of water. Under these conditions by properly regulating the current the lighter ones were carried up and the heavier ones sank to the bottom. These samples are No. 9 and No. 10 in the tables.

The second lot consists of 5 samples, Nos. 1, 3, 5, 7, and 8. The individual pearls in each sample were of the same diameter except for No. 7, which contained pearls of two sizes. These samples were obtained from Germany, and when received were coated with dye.

All of the samples were cleaned by boiling in conc. nitric acid, washing free from acid, and air drying. The diameter, surface, and volume of the pearls in each lot were determined by the method used for the sand.

Liquids.—Distilled water and a series of organic liquids were used to form the films.

Specific Gravity of Solids.—The specific gravity of the sand and the pearl samples was determined by displacement of water. A specific gravity bottle was weighed, empty, full of water, and then with a known weight of sample substituted for a part of the water. To avoid air bubbles the weighed sample was run into water in a fine stream. The bottle was then placed in a partial vacuum and let stand for several hours before the final filling and weighing was done.

Method of Determining Film Thickness.—In most of the previous work done on determining film thickness the film has been formed by subjecting the sample to the vapours of water and establishing an equilibrium at the contact surface. Usually the water vapour was at or near its saturation point. As a check on the results obtained in this way the method used in this paper was evolved, which consists in getting an equilibrium of the film, by the use of liquid water rather than vapour, and getting it with the air saturated. This would give the maximum film which could form, and at the same time would, by the magnitude of the results obtained, indicate whether there

* From the *Journal of the American Chemical Society*, *xli.*, No. 4.

was an essential difference between a film formed from the vapour and one formed from the liquid.

Considering the sand and pearl samples already described, the method involves the addition of small amounts of liquid to them, thus gradually building up on them a film of water. As successive layers of molecules are added to this film a thickness is finally reached at which the surface molecules act as normal molecules. That is they evaporate, flow, exert surface tension, &c. Any liquid beyond this amount would remain in the liquid condition. It was only necessary to get a definite test for the point at which these new properties exhibit themselves.

Apparatus.—The first and simplest arrangement used for this purpose consisted of a burette and an Erlenmeyer

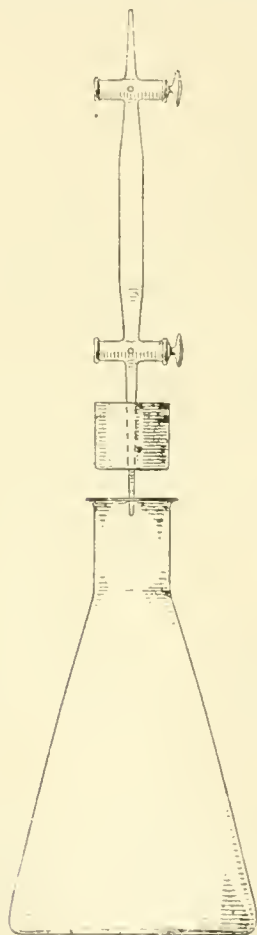


FIG. 1.

flask. The weighed sample of sand was placed in the flask and liquid added from the burette a drop at a time, with thorough shaking between, until a final drop caused the grains to stick to the flask. When this occurred water was present as free liquid. This "sticking point" was taken as the end-point of the titration.

An ordinary burette soon proved unsatisfactory for delivering the liquid, especially so in cases where the liquid was volatile. Delivering the liquid into an open flask also introduced errors with these liquids. To avoid these losses due to volatility of the liquids, and to limit definitely the volume of air saturated during a titration, a weight

burette, Fig. 1, was substituted for the ordinary burette and the liquid was delivered into a closed flask.

Procedure.—In carrying out a single determination the following procedure was used:—200 grms. of the air-dry sample was weighed and transferred to the clean dry Erlenmeyer flask. The flask was then closed by means of the stopper carrying the weight burette. The liquid was run in a drop at a time, the sand being thoroughly shaken after the addition of each drop. Towards the end of the titration only fractions of a drop were added, these being removed by tipping the flask to bring the pearls in contact with the tip of the burette.

A final addition of liquid caused a large number of the pearls to stick to the walls of the flask. The weight of the liquid used gave the amount of liquid taken up when a film of maximum thickness formed. Corrections were made in the case of volatile liquids for the amount of liquid necessary to saturate the air in the flask under the working conditions.

After a determination in which sand was used the sand was air dried and then heated to strong redness in a large platinum dish. After partial cooling it was transferred to a desiccator over phosphorus pentoxide, and kept for future determinations. The pearl samples were not ignited. They were boiled with strong nitric acid, to which some hydrochloric acid was added and were air-dried after being washed free from acid.

This procedure was followed for the purpose of determining whether a chemical reaction was involved in the holding of the liquid. If the pearls were air-dried there would be much less tendency for an unstable chemical compound to be broken down than if they were dried *in vacuo*. The intention was to have the chemical compound, if it formed at all, present at the time of titration, and not formed during it. It seemed improbable that any chemical compound formed by the methods used would decompose on exposure to ordinary conditions of temperature and pressure.

(To be continued).

OFFICERS' GUIDE TO CIVIL CAREERS.

"OFFICERS' GUIDE TO CIVIL CAREERS" is the latest book-stall pamphlet in the series issued by the Ministry of Reconstruction.

After warning employers to beware lest through their excess of caution about employing new men the best brains of the country should be tempted abroad, the pamphlet explains clearly to those seeking employment that military pay is no criterion of civil life value, and that a man must consider what his qualifications and abilities for the career he proposes adopting really are, in order to avoid setting an excessive and prohibitive value upon his services.

While many officers on demobilisation will step straight back to their work, it is obvious that the great majority will need some form of assistance to enable them to make a fair start in civil life. As suitable appointments cannot at once be found for everyone, and some may have to wait for some time before their chance comes, prudence in the disbursement of gratuity and savings is very advisable, and it is strongly urged that they should be regarded, not as pocket money, but either as capital or as an emergency fund to be drawn upon until regular work is obtained.

In addition, the Military Service (Civil Liabilities) scheme, which deals with cases of special hardship arising from service in the Forces, is to be continued for a limited period, and application for assistance may be made under this scheme by any officer or men who, having joined H.M. Forces after August 3, 1914, is unable to meet certain financial obligations and is so exposed to serious hardship, or who having previously had a business

of his own wishes to resume it, the maximum individual grant being £104.

The pamphlet describes the part played by the Appointments Department in helping to solve the Officer problem and gives a complete list of the District Branches of the Department. It gives details, too, of the scheme to provide State funds for the higher education and practical training of officers and men of educational promise.

The contemplated schemes comprise courses of higher education in Universities, Colleges, and other institutions, practical training in offices, works, and professional employments, and agricultural training at colleges or on farms. The annual sum granted will not, save in exceptional circumstances, exceed £50 for fees and £175 for maintenance.

There is also a certain limited number of appointments under the State and Local Authorities which may be suitable for ex-officers possessing special qualifications, and the main classes of such appointments and the various methods of selection are indicated.

In a section entitled "An A.B.C. of Occupations" an attempt on new lines is made to provide a brief account of a large number of professions and industries, indicating the sort of qualifications required and as far as possible the prospects offered. A section is also devoted to Overseas openings. The pamphlet, in short, seeks to give an ex-officer information or to put him on the track of information on every matter that touches on the problems of his re-settlement.

Referring to Chemistry it says:—

"This is one of the sciences on which depend many of our great manufacturing processes, such as the 'smelting' or extraction of metals from their ores and their subsequent refinement; the production of gas from coal; the manufacture of the acids; the vulcanisation of rubber; the preparation of tans for the tanning of hides; brewing; the fermentation industries and the manufacture of sugar, jam, biscuits, cattle food, soap, margarine, explosives, and artificial manures, to name but a few. There is thus a highly important chemical side to a large number of industries, for each of which a special branch of chemical technology is required. The case of dyeing is specially significant. Before the war Germany had organised the industry to a high state of perfection and exercised a virtual monopoly. The attempt to reorganise the British industry is supported by the Government, who have assisted a company known as 'The British Dyestuffs Corporation, Ltd.' It is estimated that it will take fully ten to fifteen years to reach a position even approaching that of the Germans, which was won by very hard work, by great patience, by paying close attention to the wants of their customers, and by spending large sums of money on research. For any branch of chemical industry a study of the pure science is almost indispensable. Starting from the matriculation standard, three years is normally required to obtain a B.Sc. or similar degree or diploma in chemistry, a knowledge of at least the elements of one or two other sciences being required at the same time. The minimum cost of training and maintenance may be put at about £200 a year, and the prospect is offered to any man of ordinary ability of securing an appointment on completion of his studies worth £200 to £300 a year to start with. Many chemical students who have served in the Forces seem reluctant to complete their interrupted training. The Institute of Chemistry emphatically advises them that their chances of success will depend largely on adequate preparation."

THE New Transport Company, Ltd., announce two meetings at the Caxton Hall, Westminster, S.W. 1. On Monday, June 30, at 8.30 p.m., Mr. A. W. Gattie will give an Address on his "System of Cheap Transport." On Monday, July 7, at 8.30 p.m., Mr. Roy Horniman will speak on the "Transport Bill and Housing Bill."

BOARD OF TRADE ANNOUNCEMENT.

OPENING CREDITS ON BEHALF OF ENEMIES.

THE Board of Trade have issued a General Licence under the Trading with the Enemy Proclamations authorising persons in the United Kingdom to open credits on behalf of persons or bodies of persons in enemy countries for the purpose of financing transactions that have been authorised under the trading with the Enemy legislation in the United Kingdom or any other part of His Majesty's Dominions, and transactions between persons residing or carrying on business outside His Majesty's Dominions which have been authorised by the Allied and Associated Governments or any of them.

PROCEEDINGS OF SOCIETIES.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, June 4, 1919.

Dr. SAMUEL RIDEAL, President, in the Chair.

CERTIFICATES were read for the first time in favour of Capt. John Dalton and Mr. William Norman Leng.

Certificates were read for the second time in favour of Mr. Andrew More, F.I.C., John Haworth, F.I.C., and Henry Turner Lee, M.Sc., A.I.C.

The following were elected members of the Society:—Messrs. Charles Frederick Lee Barber, A.I.C., George Stanley Withers Marlow, B.Sc., F.I.C., and Frederick William Read.

The following papers were read:—

"Examination of Commercial Samples of Nicotine." By PERCIVAL J. FRYER, F.I.C.

The author gives a review of the existing methods for the estimation of nicotine, followed by special remarks upon the refractive index as a means of estimating the amount of water present in nicotine solutions, whether the nicotine exists free or as oxalate or sulphate. The question of other possible and likely adulterants is also considered and briefly discussed.

"Mexican Insects in Poultry Food (*Notonecta*, *Corixa*, and Mexican *Cantharides*)." By T. E. WALLIS, B.Sc. (Lond.), F.I.C.

Certain poultry spices and foods contain insects either whole or powdered; these have been identified as consisting mainly of species of *Notonecta* and *Corixa* coming from Mexico. These insects form a regular article of commerce, and have also been sold under the name of "Mexican *Cantharides*."

Photographs, drawings, and descriptions of the insects are given, which will enable the analyst to identify them whole or broken.

"A Rapid Method for Determining Nickel and Cobalt in Ores and Alloys." (Part III.). By W. R. SCHOELLER, Ph.D., and A. R. POWELL.

In this, the last paper of the series, the estimation of nickel and cobalt in various alloys is described. They are precipitated by adding solid potassium iodide to a strongly ammoniacal tartrate solution. Manganese is estimated colorimetrically in the cobalt precipitate if in small quantities. If there is much manganese it must be eliminated by precipitating the nickel and cobalt as sulphides or xanthates.

"Note on the Oil of *Ceratothera sesamoides*." By E. RICHARDS BOLTON, F.I.C.

Ceratothera sesamoides, which grows on the Gold Coast, is closely allied to *Sesamum indicum*. The seeds are very similar, and so are the oils; in fact, all the analytical re-

sults which are given in the paper, with the exception of the Budouin reaction, which is negative for *Ceratotheca sesamoides*, might be given by sesame oil. The oil would be useful as edible products.

"An Improved Method for the Estimation of Nitrates in Water by means of the Phenolsulphonic Acid Reaction." By ROBERT C. FREDERICK.

Nitrates associated with chlorides up to 100 parts chlorine per 100,000 can be very accurately estimated by using a phenolsulphonic-sulphuric acid mixture made as described. The colour produced by the nitrates, which is very pure, is compared with that produced by a standard ammonia solution.

"Estimation of Morphine in Indian Opium." By JITENDRA NATH RAKSHIT and FRANK J. D'COSTA.

Two authors compare results obtained by the lime and polarimetric methods of estimating morphine in opium, and as a result of their experiments they are of opinion that the polarimetric method offers certain advantages.

GEOLOGICAL SOCIETY.

Ordinary Meeting, May 21, 1919.

Mr. G. W. LAMPLUGH, F.R.S., President, in the Chair.

The following communications were read:—

"The Silurian Rocks of May Hill." By CHARLES IRVING GARDINER, M.A., F.G.S.

The district of May Hill comprises a small area of ashy grits, which Dr. Callaway in 1900 considered to be of Pre-Cambrian age. The evidence now available does not seem to warrant any definite opinion as regards the age of these beds. Llandovery sandstones are extensively developed, and are of Upper Llandovery age. They consist of a lower division of coarse sandstones and conglomerates.

"The Petrography of the Millstone Grit Series of Yorkshire." By ALBERT GILLIGAN, D.Sc., B.Sc. F.G.S.

Since the pioneer work of Surby on this subject, published in 1859, the clastic deposits of the carboniferous system have been unaccountably neglected by petrologists. The author has followed the usual methods of investigation, and has collected a large number of pebbles and specimens from widely-separated areas which have been examined microscopically. Numerous separations of the heavy minerals have also been made from all types of rock, varying from coarse conglomerates to shales, which occur in the series.

Quartz-pebbles are dominant, and vary much both in size and in colour. The largest are found in the coarse-grained beds at the bottom and top of the series. They often show double-sphenoid forms suggestive of derivation from mechanically-deformed rocks, which inference is shown to be correct by the undulose extinction, the crenulate and mylonised structure seen when sections of them are examined in polarised light.

Blue and opalescent quartz is very common, containing inclusions often of indeterminate character arranged in streams or rows; others contain liquid with movable bubbles, while needles and hair-like inclusions are also usually present. The quartz of the finer material is similar in character, and the inclusions in the grains suggest that it has been originally derived for the greater part from such rocks as gneisses and schists.

Felspar-pebbles are abundant in all the coarse beds. They are dominantly microcline or microcline-microperthite, and, when broken, are found to be perfectly fresh, the lustre of the cleavage-faces being most remarkable. Blebs of quartz are frequently present in these felspars. In many of the rock-sections grains of microcline and oligoclase, quite fresh and unaltered, are common. Fragments showing the intergrowth of blue or opalescent quartz and microcline are fairly abundant.

NOTICES OF BOOKS.

Mnemonic Notation for Engineering Formulae. With Explanatory Notes by G. FIANDER ETCHELLS. London: E. and F. N. Spon, Ltd. New York: Spon and Chamberlain. 1918. Pp. 116. Price 6s. net.

THIS book contains the Report of the Science Committee of the Concrete Institute, with many appendices and miscellaneous articles dealing with the use of mnemonic formulae, with special reference to structural engineering. The general principles governing the selection of symbols are carefully explained, and many suggestions are made which should certainly tend to prevent chaos and confusion in the use of symbols. The author aims above all at following the obvious dictates of common sense, and in all his suggestions has kept specially in view the convenience of the reader; there is undoubtedly much truth in his criticisms of the irrelevance and even misleading nature of some symbols now employed, such as, for example, the use of *Z* for modulus, which he regards as just as logical a proceeding as suggesting the use of *M.P.* for Georgius Rex. There is possibly an unnecessary amount of repetition in the book, but the author is very anxious to emphasise his points and to make his meaning unmistakably clear, and his main arguments are undoubtedly sound and his points of view entirely sensible.

The Production and Treatment of Vegetable Oils. By T. W. CHALMERS, B.Sc., A.M.I.Mech.E. London: Constable and Co., Ltd. 1918. Pp. xi+152. Price 21s. net.

THIS book on the vegetable oil industries has been written mainly from the engineer's point of view, and the chemistry of the subject is discussed in outline only. The vegetable oil industry is rapidly developing in this country, having made remarkable strides during the last four years, and this book will certainly be welcomed by engineers and others who are finding employment arising out of its development. Although we are not yet entirely independent of foreign countries for manufactured products we are progressing favourably in that direction, and British-made margarine, for example, is now competing very successfully with the foreign product. The book provides very full and well illustrated accounts of the preparatory machinery employed in the treatment of nuts and seeds before they are taken to the oil mill proper, and oil processes of different types are described, as well as methods of extraction by chemical solvents. The advantages and disadvantages of the latter process are fully discussed, and special care is taken to refute the objections which have been raised against it and to emphasise its possible advantages. The refining of oils is treated shortly, very few accurate details of the processes employed being known outside the actual works where they are carried out. The commercial preparation of hydrogen is fully discussed in the chapter on the hardening of oils, and there is much new material in this part of the book. Short discussions of soap manufacture and the recovery of glycerin occupy the last chapters of a book which is a valuable contribution to technical literature.

The Manufacture of Aluminium. By J. T. PATTISON, F.C.S. London: E. and F. N. Spon, Ltd. New York: Spon and Chamberlain. 1918. Pp. viii+104. Price 7s. 6d. net.

THERE appears to be every likelihood of aluminium finding extensive application in the future, and as improved and cheapened methods of production are worked out and the price of the metal falls there can be no doubt that it will be used very much more universally than it is at present. The author of this book has had exceptional opportunity of making himself acquainted with modern

methods of preparing the metal, and the results of his experience will be exceedingly useful to chemists in similar positions who have still to acquire his knowledge and skill. He gives an interesting account of the evolution of modern processes from the time of Davy's earliest achievement in decomposing alumina to the Heroult and Hall processes, by which almost the whole of the world's output of the metal is now obtained. Precise details are given of the extraction of the metal by these methods, and the properties and preparation of the most important alloys are fully described, a very useful table showing the composition and uses of all the common alloys containing aluminium being included. About half the book is devoted to detailed accounts of methods of analysis employed in the study of the raw material of the aluminium industry and the commercial metal and its alloys. Those methods which in the author's experience have proved most satisfactory as regards quickness and accuracy, are described in full, and there should be no difficulty in successfully carrying out the tests and estimations, of which complete details are given.

Boiler Feed Water. A Concise Handbook of Water for Boiler Feeding Purposes. By PERCY G. JACKSON, F.I.C. London: Charles Griffin and Co., Ltd. 1919. Pp. ix+97. Price 4s. 6d. net.

IN the above modest little handbook the author sets out the results of his experiences as chemist to a Boiler Insurance Company; the material is therefore of a thoroughly practical character. In an introductory chapter the most common difficulties that are met with in the case of boiler plants are clearly explained, and the work begins with a summary of the mineral constituents of feed water and its more frequent contamination. Corrosion, a most serious danger in boilers, is discussed exhaustively, and this is followed by a chapter on Softening—Analysis of Water and of Boiler Scale. Other practical details are given, and the book concludes with an appendix of factors and other useful data. There is a good index, and the author is to be congratulated in having condensed a very large amount of sound practical information into a small bulk.

Reports of the Progress of Applied Chemistry used by the Society of Chemical Industry. Vol. III. 1918. Society of Chemical Industry, Central House, 46-47, Finsbury Square, E.C. 2.

THIS volume contains the reports on Agricultural Chemistry and Foods from the literature of the past three or four years, together with much other useful information. There are twenty-two important articles on various subjects by specialists in the particular industries, all of which are good. It is not possible here to refer to each, but Glass Refractories, by W. J. Rees, F.I.C., Metallurgy of Iron and Steel, by C. O. Bannister, F.I.C., and the Metallurgy of the Non-ferrous Metals, by G. Patchin, A.R.S.M., are of very great value at the present moment when so much development is taking place in these industries. Reports on Ceramics, Building Materials, and Fermentation are promised for the next volume, which will be awaited with interest.

NOTES.

METRIC SYSTEM IN BELGIUM.—The local Syndical Chamber for machine tools, industrial products, &c., of Liège is complaining of the difficulties caused by the almost universal British habit of quoting for goods in other than metric measures. The honorary British Vice-Consul at Liège is repeatedly having his attention drawn to the same subject, and he points out that if United Kingdom firms wish to develop their trade in Belgium quotations under the metric system are essential.

AT the Annual General Meeting of the Institution of Gas Engineers, held recently at the Institution of Civil Engineers, some remarks by Prof. Smithells on the application of Science to Industry are of such wide importance that we take the liberty of reproducing them. Referring to Scientific Principles and Practical Problems he said:—"The particular question with which I am concerned is how we shall provide the knowledge of scientific principles and their application to practical problems. It is here that I and my tribe come into relationship with the industrial world; and it is here we are apt to come into conflict. On the one hand, we have the practical man impressed with a knowledge of the realities of industry, of the immense importance of the factor of experience, of the value of native talent and sagacity—what you may almost call moral qualities—of the futility of certain kinds of learning, and of the dangers of the eager theorist. You have this practical man bent on getting what he regards as necessary from science on the strictest terms of economy in time, and with the least possible interference with what he looks upon as the real business of learning one's trade. We, on the other hand, stand with our knowledge of science, with our experience of its power of furnishing humanity with new resources, with our desire that it shall shed its full light into every corner, and with the record before us of what it has achieved for industry. We are in danger, not I think of over-estimating what it has to offer, but of under-estimating how much there is besides science which is indispensable for success in industrial callings, and our tendency is, perhaps, to undervalue education which is inherent in the prosecution of the practical calling itself. Every industry, and the gas industry among the number, can no doubt show examples of men who have by self-teaching equipped themselves with a remarkable knowledge and grasp of scientific principles. Such examples are very impressive; but I believe they have their disadvantage in tending to elevate into a prescription for all what is possible only to the very few. I think it is no exaggeration to say that at the present time you may see abundant examples in British industry of the insufficiency of self-education in science—cases where a knowledge of science and the power of using it have to some extent been acquired, but where want of the firm ground of a knowledge of basic principles is very apt to lead men astray." His remarks upon the Need of Scientific Masters were as follows:—"I think it will be generally agreed that the science teacher must come in to give his aid. And, of course, he has come in. But we must go further. I think the time has come when the gas engineer must recognise that the modern conditions of his industry demand a very much more extensive and thorough scientific training than has hitherto been customary. It is not right that I should prophesy who are going to be the highest powers for good in advancing the gas industry—the man of affairs, the manager, the engineer, or the chemist. But I think that no one can do that that the industry does need, and will need more and more, an accession to its ranks of men who are really scientific masters of their profession. The science that ministers to your calling is not less comprehensive than that required for any other branch of engineering. The mechanical, civil, and electrical engineers feed their profession with a constant stream of recruits who have had a three or four years' course at a University; and I feel certain that gas engineers should come into line. This will no doubt seem a large demand; but I am satisfied that nothing less will suffice. The view that all essential knowledge of science for the gas engineer is to be obtained in spare hours of the working day by study, by attendance at evening classes, or by short intensive courses, cannot be entertained. I have no desire to belittle such forms of education. They may be made good and useful so far as they go; but they cannot possibly provide all that is needed. I would most earnestly entreat the members of the industry not to be beguiled by half-measures, but to make bold educational investments. I do not look for a sudden change of

attitude, nor do I expect to exercise much influence on a great many individuals. I do not foresee a rush to the Universities; but I do sincerely hope that those who have the faith and courage will make a beginning upon a real professional education conformable to the needs of the industry and the present state of scientific knowledge."

CANADIAN NATIONAL EXHIBITION AT TORONTO.—Information has been received from His Majesty's Trade Commissioner at Toronto (Mr. Field) to the effect that it is proposed to obtain space at the Canadian National Exhibition, to be held at Toronto during the last week of August and the first week of September next, for a Bureau of Information in connection with the Trade Commissioner Service in Canada. Mr. Field has expressed a desire to display the catalogues and other trade publications of United Kingdom firms at the Bureau in question, and it is suggested that catalogues, &c., of the following lines would be useful for the purpose:—Textile machinery; crockery, glass, &c.; industrial machinery, including pulp and paper machinery, and supplies; electrical machinery, appliances, and equipment; shipbuilding machinery and supplies; mining machinery and supplies; heavy machine tools; electrical railway equipment; motor vehicles; chemical plant, &c.; scientific instruments; sugar machinery. Manufacturers and others who wish to avail themselves of this opportunity of having their catalogues brought to the notice of Canadian firms at the Exhibition should communicate with Mr. Field direct, enclosing copies of their catalogues and other trade publications for display at the Bureau at the above-mentioned Exhibition. The catalogues, &c., should be received by Mr. Field—whose address is 257–260, Confederation Life Buildings, Toronto—not later than August 15 next.

DIAMONDS were discovered in Brazil in the year 1728, and since that time until the present intermittent supplies of Brazilian diamonds have been secured, chiefly from river washings. It has recently been reported that the source of these stones has been traced to "pipes" similar in character to the well-known African deposits; one pipe is reported to be several square miles in extent! A company has been formed to work the property, and the results will be looked forward to with interest.

THE export of zirconia from Brazil to the United States, Great Britain, and Japan has grown very considerably; the figures for 1918 show an export of 2,141,182 kilos.

CASEIN WATERPROOF GLUE.—(H. A. Gardner, *Aircraft Technical Note No. 46*, Navy Department, U.S.A., Bureau of Construction and Repair).—The Forest Service has recently completed some very extensive tests with casein glue. These tests have demonstrated that there are now available, commercially at least, three brands which are all furnished by the makers in the form of dry compounds to be mixed with water. These glues are to be considered waterproof in the sense that they are not dissolved out or injured by water. Permanently prolonged soaking causes such glues to soften and become weak, but upon subsequent redrying they regain their former strength. The principal difficulty with these glues is in their rapidity of setting after being mixed with water; from two to five hours is the longest period of fluidity. Experimental batches of casein glue, to which certain materials have been added to delay the set, have, however, remained fluid and workable for periods as long as forty-eight hours. Attempts have been made to determine what percentage of bad joints would occur in using casein glue. Every one of about 200 specimens made by ordinary mechanics was found satisfactory. It is believed that, if the instructions of the manufacturers are followed, casein glue is a safer material for aircraft construction than hide glue. It appears, therefore, for strength members in aeroplanes, that these glues should be used in place of hide glue.—*Journ. Franklin Institute*, May, 1919.

Assistant Assayer (aged 23 to 27) required at once. Experience in Assaying Gold and Silver essential. Permanency; good prospects. State age, experience, and salary required.—Address, "A 23," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Chemist, three years' experience in large Tar Products Works, before taking active service, now demobilised, desires Employment in London or the Provinces.—Address, T. T. CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Chemist wanted for Cotton Dyeing and Mercerising establishments in Scotland. State experience, age, and salary expected.—Address, C. D., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Wanted in a London Laboratory, a Junior Chemical Assistant. Give particulars of training and salary required.—Address, "A," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Youth (17), good knowledge of Chemistry, seeks Employment in Laboratory.—Address, A. H., 1, Phoenix Lodge Mansions, Hammersmith, W.

Young man (31), with good knowledge of Chemistry and Engineering practice, desires Situation at living wage with Chemical Engineering firm, or Assistantship in Works Laboratory of progressive firm which appreciates intelligent and willing service.—Address, Sharpe, 7, Toll Road, K. near Gardine on-Forth

BIRKBECK COLLEGE, LONDON.

ASSISTANT LECTURER IN CHEMISTRY.

The Governing Body invite applications for the above appointment. Commencing salary £220 to £250 (according to experience and qualifications), with regular increments.—Applications to THE SECRETARY, Birkbeck College, E.C. 4, from whom further particulars may be obtained.

UNIVERSITY OF ABERDEEN.

CHAIR OF CHEMISTRY.

The CHAIR OF CHEMISTRY, in the patronage of the University Court, becomes vacant by the resignation of Professor SONNY on September 30th next. The salary is £900 per annum.

Applications for the office, together with 16 copies of testimonials, should be lodged with the SECRETARY of the University on or before JULY 5.

STAFFORDSHIRE EDUCATION COMMITTEE

BRIERLEY HILL HIGHER EDUCATION COMMITTEE

Applications are invited for the Post of HEAD MASTER of the Technical School, Brierley Hill, South Staffordshire

Experience in Teaching and acquaintance with the Iron and Steel Trades, or with the Chemistry of Refractory Materials, desirable.

Initial salary £300 a year.

Further particulars and forms of application may be obtained from the undersigned. Applications must be received not later than JUNE 30, 1919.

GRAHAM BALFOUR,

County Education Offices,
Stafford, June, 1919.

Director of Education

If in good condition, Sixpence per copy will be paid for any of the undermentioned numbers of the CHEMICAL NEWS which may be forwarded to this office:—

3052, December 6th, 1918.

3066, January, 17th, 1919

3068, January 31st, 1919.

3069, February 7th, 1919.

3070, February 14th, 1919.

3075, March 21st, 1919.

16, NEWCASTLE STREET, FARRINGTON STREET, LONDON, E.C. 4

THE CHEMICAL NEWS

VOL. CXVIII., No. 3089.

THE ALLOTROPY OF CARBON.

By MAURICE COPISAROW.

THE application of the theory of allotropy (see CHEMICAL NEWS, cxviii., 265) propounded in general terms for all the elements, to a single characteristic case—the element carbon necessitates our dealing with the valency of the carbon atom and the complexity and varieties of the carbon molecules.

In the light of the chemistry of carbon compounds the carbon atom can be regarded as potentially always tetravalent, as carbon monoxide, carbon compounds containing double or triple bonds, the triphenyl methyl series, and the poly-methylene group in no way undermines the conception of such potential tetravalency.

The polyatomicity of a carbon molecule is proved by—

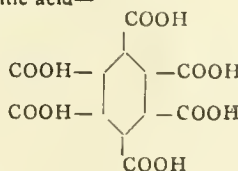
1. The existence of several forms of carbon, chemically and physically distinct from one another.
2. The high volatilisation-point of carbon.
3. The general theory of the solid state.
4. Products of moist oxidation.
5. Combustion of carbon (Rhead and Wheeler, *Trans.*, 1910, xcvi., 2181; 1911, xcix., 1140; 1913, ciii., 461).
6. The X-ray spectro-metric study of the modifications of carbon (Debye and Scherrer, *Phys. Zeit.*, 1916, xvii., 277; 1917, xviii., 291; Oie and Eyl, *Proc. K. Akad. Wetens. Amsterdam.*, 1917, xix., 920).

Not only has the polyatomicity of carbon molecules been assumed, though more or less tacitly, but attempts have also been made to study the complexity of the molecules and to establish the constitutional molecular formula of one or more of the forms of carbon.

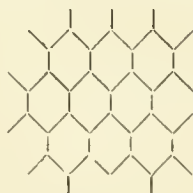
Kekulé (*Zeit. Angew. Chem.*, 1899, p. 950) regards a molecule of amorphous carbon as consisting of 12 atoms.

Barlow and Pope (*Trans.*, 1906, lxxx x., 1742) suggested the possibility of a tetrahedron and triphenylene configuration for a carbon molecule (see Figs. 1. and 4a).

Dewar (CHEMICAL NEWS, 1908, xcvi., 16) proposed a concentric ring formula, somewhat modified by Redgrave and Tomlinson (CHEMICAL NEWS, 1908, xcvi., 37). Dewar based his view on the moist oxidation of amorphous carbon to mellitic acid—



Aschan (*Chem. Zeit.*, 1909, xxxiii., 561), criticising Dewar's suggestion, put forward a formula, which can be regarded as an extension of the triphenylene representation by Barlow and Pope (*loc. cit.*)—



Dimroth and Kerkovius (*Ann.*, 1913, cccxcix., 120) conclude from their study of the oxidation of carbon the carbon molecule to consist of pentagons as well as hexagons.

Bragg (*Proc. Roy. Soc.*, 1913, A, 610), studying the crystalline structure of diamond by means of the X-ray spectrometer, advanced a three-dimensional configuration for the structure of the diamond (see Fig. 2).

(In connection with the X-ray spectrometric method of investigation of crystalline structures attention may be drawn to the work of Moseley—*Phil. Mag.*, 1913, VI., xxvi., 1024; 1914, VI., xxvii., 703; Barlow—*Proc. Roy. Soc.*, 1914, A, 623; and Ewald—*Phys. Zeit.*, 1914, xv., 309).

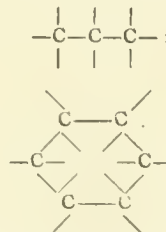
Hans Meyer (*Monats.*, 1914, xxxv., 163), discussing the carbon "molecule," puts stress upon the difficulty, if not futility, of trying to define the chemical entity of the three forms of carbon.

Debye and Scherrer (*loc. cit.*) conclude from the Laue-graphs of their modified X-ray spectrometric method of study, that diamond and graphite are the only two distinct forms of carbon, amorphous carbon being apparently simply finely divided graphite. They assign a tetragonal configuration to diamond and a trigonal to graphite. It is clear from the above that a method of investigation so general as to be applicable to all forms of carbon has not yet been proposed.

Whilst the method of moist oxidation can be applied more or less successfully to amorphous carbon and to some extent to graphite, the X-ray method is confined to diamond with a somewhat strained extension to graphite.

Now, if we consider the problem from the point of view of linkages, i.e., of molecular structure in the light of the theory of allotropy, we secure a general method of investigation, embracing all forms of carbon, a method capable of extensive experimental verification on the basis of all the known chemical and physical properties. Investigating all possible representations of the structure of a carbon molecule we find that these possibilities resolve themselves into three fundamentally distinct classes or groups.

1. A non-rigid molecular configuration, some valencies of which are free—



(See also Fig. 1).

- II. A rigid molecular configuration, some valencies of which are free (see Fig. 3).

- III. A rigid molecular configuration, all valencies of which are fixed (see Figs. 4a, 4b, and 2).

Thus on theoretical grounds we expect to find in the case of carbon not more than three distinct allotropic forms, a conclusion in striking agreement with facts; i.e., the existence of three forms of carbon—amorphous carbon, graphite, and diamond.

The several new modifications (graphitoid, &c.) of carbon suggested by Brodie, Berthelot, Luzi, and others have been proved to be either compounds or solutions and mixtures of carbon with some other elements.

(See Porcher, CHEMICAL NEWS, 1881, xlv., 203. Bartoli and Papasogli, *Gazz.*, 1882, xii., 113; 1883, xiii., 37; 1885, xv., 445. Moissan, *Comptes Rendus*, 1893, cxvi., 609; 1894, cxix., 976; 1895, cxx., 17; cxxi., 540; *Ann. Chim. Phys.*, 1896, VII., viii., 289, 306, 466. Wiesner, *Monats.*, 1892, xiii., 371. Weinschenk, *Zeit. Kryst. Min.*, 1897, xxviii., 291. Hyde, *Journ. Soc. Chem. Ind.*, 1904, xxiii., 300. Trener, *Fahresb. Geolog. Reichs. Wien.*, 1906,

405; *Zeit. Kryst. Min.*, 1909, xlv., 124; Charpy, *Comptes Rendus*, 1907, cxlv., 1173; 1909, cxlviii., 920. Le Chatelier and Wologdine, *Comptes Rendus*, 1908, cxlv., 491.

Debye and Scherrer's (*loc. cit.*) unification of amorphous carbon with graphite is untenable as it is in complete disagreement with all the chemical and physical properties of these two forms. No matter how finely divided the graphite may be (Acheson's or "colloidal" graphite) its behaviour towards moist oxidants, its products of oxidation, mode of combustion, and physical properties all greatly differ from those of amorphous carbon.

Koblschutter's (*Zeit. Anorg. Chem.*, 1919, cv., 35, 121) effort to prove amorphous carbon and graphite to be physical forms of "black carbon," thus agreeing with Debye and Scherrer's (*loc. cit.*) conclusion, appears to be decidedly strained, ignoring as it does the more distinct chemical and physical differences of these two forms of carbon, the conditions of transition and the possibility of the "intermediary stages" being simply mixtures of graphite with amorphous carbon.

H. Meyer (*loc. cit.*) and H. Meyer and Steiner (*Monats.*, 1914, xxxv., 475), recording the dependence of the yield of mellitic acid from charcoal upon the latter's source and temperature of carbonisation, express some doubt as to the entity of the carbon "molecule" and the close connection of its constitution with the product of oxidation.

But we must remember that deductions depend often more upon the character of interpretation of certain experiments than the experimental evidence itself. The yield of mellitic acid does vary with the source of the charcoal employed and the temperature, pressure, and duration of carbonisation, but the formation of the mellitic acid cannot be attributed to the presence of complex hydrocarbons, possibly retained by the charcoal carbonised at a comparatively low temperature, as a quantitative determination of the percentage of hydrogen, oxygen, and nitrogen invariably accompanying this kind of charcoal gives not more than 1 per cent of these gases, whilst the yield of mellitic acid reaches as high a value as 40 per cent. The dark residue "mellogen" (Bartoli and Papasogli, *loc. cit.*; Dickson and Easterfield, *Proc. Chem. Soc.*, 1898, 163), remaining after the first oxidation, gives on exhaustive oxidation again mellitic acid and also some oxalic acid.

To attribute the varying yield of mellitic acid to the existence of several modifications of amorphous carbon, as some investigators are inclined to do, is quite unwarranted as such an explanation of the somewhat varying quality and properties of charcoal would necessitate the assumption of a whole series of modifications of amorphous carbon, corresponding to every source of charcoal and practically to every 20—50° of temperature of carbonisation.

The causes of the dissimilar behaviour of various samples of charcoal are probably much simpler and nearer at hand. Such causes may be:—

1. A high temperature of carbonisation, which, reducing the porosity of the resulting amorphous carbon or charcoal, increases in consequence its resistance to oxidation.
2. A high temperature of carbonisation facilitates the conversion of amorphous carbon into graphite, so that we may deal with charcoal containing a high percentage of finely divided graphite (Arsem, *Trans. Am. Electrochem. Soc.*, 1911, xx., 105).
3. A high percentage of mineral matter contaminating charcoal may affect its properties in more than one way. Thus we find that there are three distinct allotropes of carbon corresponding to the three, theoretically possible, fundamentally different configurations.

The following considerations may serve as a pioneer attempt to assign to each modification its constitutional formula.

The calorimetric measurements of the heat of complete

combustion of carbon per grm.-atom give the following numbers (Berthelot and Petit, *Ann. Chim.*, 1889, VI., xviii., 89, 98):—

	Cals.
Amorphous carbon	97650
Graphite	94810
Diamond	94310

These figures indicate the sum total of the energy liberated during the formation and degradation of the possible complexes (Rhead and Wheeler, *loc. cit.*) plus that of the oxidation of the carbon monoxide to carbon dioxide.

(It must be noted that the calorimetric measurements of the heat of combustion of the modifications of carbon differ considerably with every experimenter. Compare data of Favre and Silbermann, *Ann. Chim.*, 1852, III., xxxv., 357; Berthelot and Petit, *loc. cit.*; Mixer, *Am. Journ. Sci.*, 1905, IV., xix., 440; and Roth and Wallasch, *Ber.*, 1913, xlv., 896).

Taking equal weights of amorphous carbon, graphite, and diamond, and subjecting them to complete combustion, we find that the amount of heat evolved is different for each form of carbon, although the number of atoms taken and the number of CO₂ molecules formed is identical.

Looking for the cause of this dissimilarity of thermic values we are driven to attribute it to the different stability of the molecules in the three cases, which must depend upon the mode of linkage of the units constituting the molecule as well as the complexity of the molecule itself.

Returning to our classification of theoretically possible configurations we expect that the least stability will be exhibited by molecules whose units have the power of free rotation, or, in other words, which have free valencies; the maximum stability will be found in the molecule all the constituent units of which are in a state of rigidity and all valencies fixed; the intermediate case being a molecule having some valencies free, but a rigid structure. Now, considering the fact that the greater the stability the smaller will be the evolution of heat on complete combustion (compare the case of phosphorus), and correlating this with the calorimetric measurements quoted above, we find that—

Amorphous carbon is represented by Class I., where none of the atoms are rigid.

Graphite, Class II., the atoms are rigid but some valencies free.

Diamond, Class III., all atoms are rigid and all valencies fixed.

These deductions find strong support in the character of the products of the moist oxidation of carbon.

The molecule of amorphous carbon with none of its units rigidly fixed, as might be expected, is the least resisting to oxidants and yields mellitic acid. Graphite with its partially fixed units gives rise to graphitic oxide or acid, an acid more complex than mellitic. The rigidly fixed units of diamond are practically unaffected under the same conditions of oxidation. (V. Meyer—*Ber.*, 1871, iv., 801; *Ann.*, 1875, cxlxxx, 175. Schulze—*Ber.*, 1871, iv., 802, 806. Standenmaier—*Ber.*, 1898, xxxi., 1481; 1899, xxxii., 1394, 2824. Dickson and Easterfield—*loc. cit.* Meyer and Steiner—*loc. cit.*)

It would appear to be very probable, on the basis of the theory of the constitution of the three types of carbon advanced above, that the values of any selected physical property should show a regular gradation from amorphous carbon to the diamond, the value for graphite lying between the values for the two other forms. If we find that such a gradation appears when a number of physical properties are taken, we can say that this behaviour is consistent with the hypothesis on which the present discussion is based, and it may therefore in this sense be regarded as affording evidence confirming the hypothesis.

Below are collected the values for a number of physical constants, which have been determined for all three forms

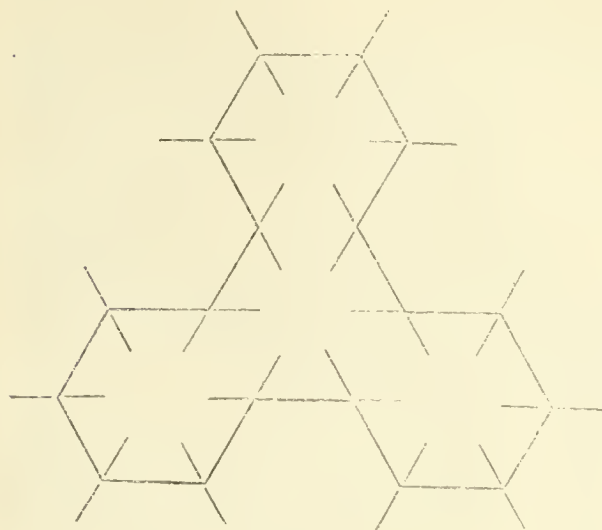


FIG. 1.

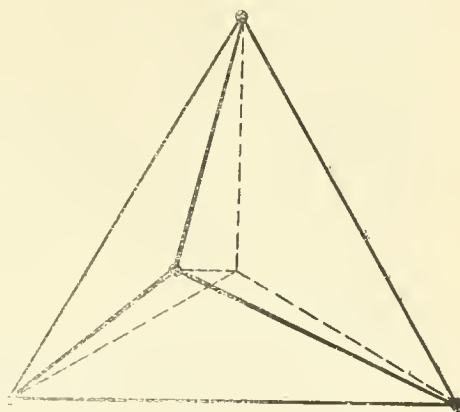


FIG. 3.

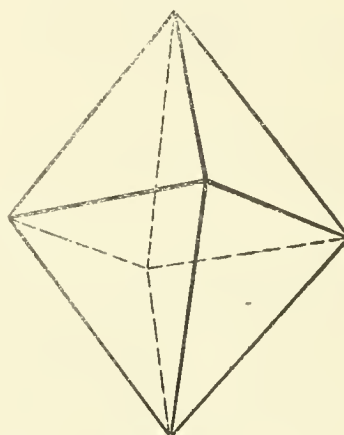


FIG. 4 a.

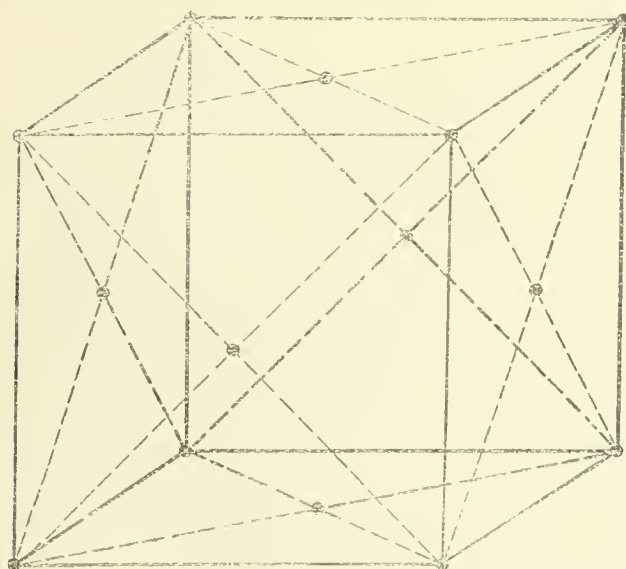


FIG. 2.

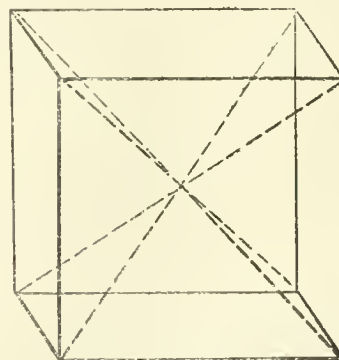


FIG. 4 b.

of carbon. The numbers are taken from Landolt Börnstein, "Tabellen," 4th edition, 1912.

1. Density.

Diamond	..	..	..	..	..	..	..	3.51
Graphite	..	..	..	..	..	..	..	2.10-2.32
Amorphous carbon—								
Gas coke	..	..	..	..	..	..	..	1.885
Cocoanut-charcoal	..	..	..	..	..	..	..	1.67-1.860
Lampblack, sugar-charcoal, and wood-charcoal	..	..	..	..	..	..	..	1.70-1.80

2. Coefficient of Cubical Expansion.

Diamond	..	..	..	..	..	..	..	0.00000375
Graphite	..	..	..	..	..	..	..	0.0000104
Gas coke	..	..	..	..	..	..	..	0.0000162

3. Thermal Conductivity.

Diamond (0° C.)	..	..	..	..	..	..	0.33 (a)
Graphite	..	..	..	..	..	..	0.0117
Charcoal	..	..	..	..	..	..	0.000405

(a) Eucken, *Phys. Zeit.*, 1911, xii., 1005.

4. Specific Heats.

(All measured by Weber Pogg. Ann., 1875, cliv, 367, 553).

Diamond (10° C.)		0.1128
Ceylon graphite (10° C.)		0.1604
Wood charcoal (0°—24° C.)		0.1653

5. Electrical Conductivity.

Diamond (15° C.)		0.211·10 ⁻¹⁴
		0.309·10 ⁻¹²
Graphite (15° C.)		0.082·10 ⁴
Charcoal (12° C.)		0.25

An inspection of this table shows that, with the single exception of the electrical conductivity, all the physical properties are in the order we should expect. In the case of the electrical conductivity, graphite occupies an anomalous position, in that its conductivity is very much larger than that of either the diamond or amorphous carbon. In this connection two facts appear to be important. First, the value of the electric conductivity of graphite is so very much larger than those of the other two forms that it would lead one to suspect that it is occasioned by something quite different from the mode of linkage of the carbon atoms in the different forms of carbon, since we could scarcely expect that the differences in the atomic linkage would change a substance which is an insulator, like the diamond, into a substance which is a metallic conductor, like graphite. And, secondly, we can see that there is a real anomaly in the case of graphite, because the thermal conductivities are in the order expected, and thence, from the law of Wiedemann and Franz, which states that the ratio of the thermal and electrical conductivities is (at least in the case of metals—Eucken, *loc. cit.*) approximately constant, we should also expect the electrical conductivities to be in the same order.

The abnormal electrical conductivity of graphite is, in fact, a property which still awaits explanation.

The suggested configurations of the allotropes of carbon are also in agreement with the "cyclic condensations" of carbon by Rousseau (*Comptes Rendus*, 1893, cxvii., 164) and Ludwig (*Chem. Zeit.*, 1901, xxv., 979; *Zeit. Elektro. Chem.*, 1902, viii., 273), the crystalline structures of diamond and the conclusions of Barlow and Pope (*loc. cit.*), and Bragg (*loc. cit.*), and Debye and Scherrer (*loc. cit.*). The elucidation of the molecular structure of the carbon allotropes throw much light upon the mechanism of the combustion of carbon, a problem which has received a good deal of attention.

Under the stress of experimental evidence the reduction theory of Lang (*Zeit. Phys. Chem.*, 1888, ii., 62) has been replaced by that of gradual oxidation by Baker (*Phil. Trans.*, 1888, A, clxx x, 571) and Dixon (*Trans.*, 1890, lix., 774; 1899, lxxv., 630), which in its turn is being substituted by the theory of complexes, proposed by Rnead and Wheeler (*Trans.*, 1910, xviii., 2181; 1911, xcix., 1140; 1913, ciii., 461).

The conception of a non-rigid configuration for amorphous carbon, containing free valencies, affords a complete explanation of—(1) The comparative easy combustibility of this form of carbon; and (2) The simultaneous evolution of CO and CO₂, products of disruption of the complexes, logically constituting the first stage of oxidation.

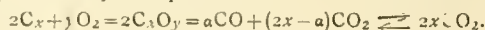
The conception of a rigid configuration for diamond and graphite explains the considerable resistance to combustion exhibited by these allotropes, and suggests that no intermediate complexes, assumed in case of amorphous carbon, are likely in the course of combustion of diamond and graphite.

These possibilities present themselves as representing the mechanism of the combustion of diamond or graphite:—(1) Their molecular structures disintegrate at the exceedingly high temperature of its combustion; or (2) It is primarily converted into amorphous carbon (with

or without passing through the graphite form in case of diamond, and then pass through the stages indicated for amorphous carbon).

In the light of the work of Moissan (*Comptes Rendus*, 1897, cxxiv., 653), Crookes (*Proc. Roy. Soc.*, 1904, A, lxxiv., 47), and Vogel and Tammann (*Zeit. Phys. Chem.*, 1909, lix., 598) on the transformation of diamond into graphite, and the work of Berthelot (*Comptes Rendus*, 1902, cxxxv., 1018), Parsons and Swinton (*Proc. Roy. Soc.*, 1908, A, lxxx., 184), and Swinton (*Proc. Roy. Soc.*, 1909, A, lxxxii., 176) on the conversion of diamond into amorphous carbon, the second hypothesis appears to be the more probable one; the transformation of diamond and graphite into amorphous carbon preceding the process of oxidation.

With reference to the combustion of amorphous carbon, whilst the number of theoretically possible complexes is obviously large, the general progress of reaction and final complexes, judging by the ultimate products, can be represented by the equation—



Where x is the number of atoms in a molecule of amorphous carbon, y equals $\frac{1}{2}(4x - \alpha)$, and α is a variable, depending upon temperature, pressure, and concentration of oxygen and varying between $2x$ and zero.

A CONVENIENT METHOD OF ANALYSIS OF FLUORSPAR AND OF BASIC SLAGS CONTAINING FLUORINE.

By Lieut. G. R. DOYLE.

THE author believes that the following method, now published for the first time, will readily commend itself as being in several ways more advantageous than existing processes.

The sample is finely powdered in an agate mortar, and 0.5 gm. is weighed out into a porcelain, silica, or platinum dish. A little water is added to form a paste, and 25 cc. of glacial acetic acid, and the mixture evaporated nearly to dryness on the water-bath, with occasional stirring. The assay is now treated again with 25 cc. of glacial acetic acid, and evaporated completely dry, all free acetic acid being driven off in the steam-oven. The residue is now taken up with a little hot water, transferred to a small beaker, diluted to 80 cc., and boiled for ten minutes, or until the residue on standing a few minutes shows a clear supernatant liquid. If a colour persists, through the presence of acetic acid, the sample is diluted with 20 cc. of water and boiled again.

(NOTE.—If a large amount of iron be present, or the sample be rather dark in colour, the residue after filtering must be washed back into the previously used dish, and treated again with glacial acetic acid, evaporated to dryness as before, transferred to a beaker, boiled with water, and filtered. The filtrates are combined).

Residue contains:—

- All lime existing as CaF₂.
- The greater part of the silica.
- All iron and alumina.

Filtrate contains:—

- Soluble or available lime (CaO and CaCO₃).
- Soluble silica.
- Manganese.
- Magnesia.
- Lead.

Examination of Residue.

Residue is ignited in a weighed platinum dish (but not so strongly as to decompose CaF₂), cooled, and weighed until constant in weight; treated with H₂F, and evaporated to dryness on water-bath, ignited, and weighed. Loss = SiO₂.

The remaining residue is increased by 5 cc. H_2SO_4 , evaporated until the formation of fumes, and finally ignited and weighed again. Gain = increase of CaSO_4 over CaF_2 . $\text{CaSO}_4 \times 0.5735 = \text{CaF}_2$.

The residue is boiled for twenty minutes with 20 cc. HCl , transferred to a beaker, increased by ammonium chloride and ammonia, boiled, and filtered. If much Fe and Al are present precipitation is carried out again. The residue of Fe and Al is ignited, weighed, and deducted from the combined weight of Fe + Al + CaF_2 . Difference = CaF_2 .

If lead be present H_2S is passed before precipitation of the iron and aluminium.

After Fe and Al have been weighed the assay is dissolved, reduced, and titrated, the Al being thence determined by difference.

Examination of Filtrate.

The filtrate is evaporated to dryness with 5 cc. HCl and three drops HNO_3 , baked, taken up in 5 cc. HCl , diluted, and filtered. The silica now obtained is added to that found in the residue.

Ammonium chloride solution, bromine to saturation, and excess of ammonia are added to this filtrate, which is boiled, filtered, and, ignited. MnO is calculated from the Mn_2O_3 obtained. Factor, 93.01. (If lead be present it is eliminated by H_2S prior to precipitation of Mn).

The filtrate is increased by ammonium oxalate, boiled, allowed to settle, and filtered. The precipitate, which consists of available lime, is strongly ignited and weighed as CaO .

Magnesia in the filtrate is precipitated with ammonium phosphate, and left overnight to settle.

GALLIUM.*

By L. M. DENNIS and J. ALLINGTON BRIDGMAN.

(Concluded from p. 292).

A STUDY OF CERTAIN SALTS OF GALLIUM.

Gallium Selenate.

A solution of gallium selenate was prepared by placing gallium hydroxide in an amount of selenic acid insufficient to dissolve all of the hydroxide and heating the acid nearly to boiling. After several hours of digestion the solution was freed from the excess of gallium hydroxide by filtration, and the filtrate was evaporated at room temperature. The crystals that separated were drained on a Witt plate by suction. The salt is very soluble, and it is difficult to obtain crystals that are satisfactory for microscopic examination. The crystals show oblique extinction, and they therefore belong either to the monoclinic or to the triclinic system.

The salt was dried to constant weight in the air and was then analysed. Selenium was determined by placing a weighed sample of the salt in concentrated hydrochloric acid and heating this to boiling to reduce selenic acid to selenious acid. The selenious acid was then reduced to free selenium by passing sulphur dioxide through the hot solution. The precipitated selenium was collected on a weighed Gooch crucible and was dried at 110° and weighed. Gallium was determined in the filtrate by the sodium sulphite method.

Calculated for $\text{Ga}_2(\text{SeO}_4)_3 \cdot 16\text{H}_2\text{O} - \text{Ga}_2\text{O}_3$, 21.90; SeO_3 , 44.49; H_2O , 33.61. Found Ga_2O_3 , 21.77, 21.66, average 21.71; SeO_3 , 44.49, 44.24, average 44.36; H_2O , by difference, 33.98.

When the sample of the crystalline gallium selenate was dried in the air 2.5145 grms. of the salt lost 0.2810 gm., which corresponds to 5.94 molecules of water. Consequently, the salt that was dried by suction contains about 22 molecules of water. (The same degree of hydration, namely, 22 molecules of water, was found to exist in a sample of gallium sulphate that was dried by simply pressing the crystals between sheets of filter-paper).

These results indicate that a hydrate of gallium selenate containing 16 molecules of water exists, and that it is also probable that when gallium selenate crystallises from aqueous solution at room temperature the salt contains 22 molecules of water of crystallisation.

The solubility of this air-dried crystalline gallium selenate was determined by placing an excess of the salt in water in a stoppered bottle, heating the contents of the bottle to 25° in a thermostat for six hours and then pipetting off samples of the supernatant saturated solution and weighing them. The gallium in these samples was determined by the sodium sulphite method.

Weight of saturated solution taken (grm.) 0.7558 0.6192
Weight of Ga_2O_3 found (grm.) .. 0.0908 0.0749

The average of these values is 0.1205 gm. of Ga_2O_3 per gm. of solution. One part of the salt therefore dissolves in 1.74 parts of water at 25° , and 100 cc. of the solution contains 57.58 grms. of gallium selenate.

Cæsium Gallium Selenate Alum.

A solution containing gallium selenate, cæsium selenate, and some free selenic acid was evaporated at room temperature. The crystals were separated from the mother-liquor and were dried in the air. They showed the octahedral form characteristic of the alums.

Cæsium was determined by precipitation with chloroplatinic acid, selenium by precipitation as free selenium, and gallium by precipitation with ammonium sulphite in the filtrate from the selenium determination. The water of crystallisation was determined by drying a sample of the salt to constant weight at about 180° .

Calculated for $\text{CsGa}(\text{SeO}_4)_2 \cdot 12\text{H}_2\text{O} - \text{Cs}_2\text{O}$, 19.96; Ga_2O_3 , 13.31; SeO_3 , 36.07; H_2O , 30.65. Found $-\text{Cs}_2\text{O}$, 19.78; Ga_2O_3 , 13.33; SeO_3 , 35.73; H_2O , 30.33.

These results show that the salt has the formula $\text{CsGa}(\text{SeO}_4)_2 \cdot 12\text{H}_2\text{O}$ and that it is therefore a typical alum.

The solubility of this alum in water at 25° was determined in the manner described under the selenate.

Weight of saturated solution taken (grms.) 2.0702 2.0422
Weight of Ga_2O_3 found (grm.) .. 0.0109 0.0109

The average of these results is 0.0053 gm. of Ga_2O_3 per gm. of solution. One part of the salt therefore dissolves in 24.1 parts of water at 25° , and 100 cc. of the solution contains 4.15 grms. of the alum.

Ammonium Gallium Sulphate Alum and Cæsium Gallium Sulphate Alum.

During the process of extraction of germanium from certain material in this laboratory there were obtained residual solutions that were rich in zinc sulphate, and that contained about 30 per cent of sulphuric acid. Spectroscopic examination of these solutions showed the presence of gallium.

Lecoq de Boisbaudran separated traces of indium from gallium by utilising the fact that ammonium gallium alum is quite insoluble in 70 per cent alcohol (*Comptes Rendus*, 1882, xcvi., 410). It therefore seemed probable that separation of this alum from alcoholic solution might furnish a convenient means for the recovery of gallium from such residues as those above mentioned. The development of such a method made necessary the determination of the approximate solubility of ammonium gallium alum and of the corresponding cæsium alum

* This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by J. Allington Bridgman in partial fulfilment of the requirements for the degree of Doctor of Philosophy. From the *Journal of the American Chemical Society*, xl., No. 10.

would doubtless be even less soluble a sample of that compound was prepared and its solubility was determined.

A sample of each of these two alums was placed in a small bottle, an amount of water insufficient to completely dissolve the sample was added to each, and the mixture held at 25° in the thermostat for six hours. The gallium present in weighed amounts of the saturated supernatant solution was then determined.

The solubilities were then determined for each of the alums, using first 50 per cent alcohol and next 70 per cent alcohol. After the mixture had been held in the thermostat at 25° for six hours, 40 cc. of the supernatant liquid was pipetted off in each case and was evaporated to dryness. Each residue was then heated for two hours at 150° and was weighed as the mixture of the anhydrous sulphate of gallium with ammonium sulphate or with caesium sulphate. The solubilities of each of the alums in a mixture of 35 cc. of water, 50 cc. of absolute ethyl alcohol, and 15 cc. concentrated hydrochloric acid was then determined. The gallium in samples of 40 cc. of the saturated supernatant solution was precipitated by the sodium sulphite method. The results of these various determinations follow:—

Solubility of Ammonium Gallium Sulphate Alum.

1. In water.

Weight of saturated solution taken (grms.) 1.0248 0.7010
Weight of Ga_2O_3 found (grm.) .. 0.0463 0.0309

The average of these values is 0.0446 grm. of Ga_2O_3 per gm. of solution. One part of the salt therefore dissolves in 3.24 parts of water at 25°, and 100 cc. of the solution contains 30.84 grms. of the alum.

2. In 50 per cent alcohol. 40 cc. of the saturated solution of the alum gave a residue that weighed 0.0049 grm., which corresponds to 0.0411 grm. of Ga_2O_3 or 0.2170 grm. of ammonium gallium alum per litre of solution. One part of the salt therefore dissolves in 4600 parts of 50 per cent alcohol at 25°, and 100 cc. of the solution contains 0.0217 grm. of the alum.

3. In 70 per cent alcohol. 40 cc. of the saturated solution of the alum gave a residue that weighed 0.0020 grm., which corresponds to 0.0166 grm. of Ga_2O_3 or 0.0875 grm. of ammonium gallium alum per litre of solution. One part of the salt therefore dissolves in 11,400 parts of 70 per cent alcohol at 25°, and 100 cc. of the solution contains 0.00875 grm. of the alum.

4. In a solution containing 35 cc. of water, 50 cc. of absolute alcohol, 15 cc. of concentrated sulphuric acid. 40 cc. of the saturated solution of the alum yielded 0.0122 grm. of Ga_2O_3 , which corresponds to 0.305 grm. of Ga_2O_3 or 1.613 grm. of ammonium gallium alum per litre of solution. One part of the salt therefore dissolves in 620 cc. of this solution at 25°, and 100 cc. of the solution contains 0.1613 grm. of the alum.

The Solubility of Caesium Gallium Sulphate Alum.

1. In water.

Weight of saturated solution taken (grms.) 2.0812 1.7305
Weight of Ga_2O_3 found (grm.) .. 0.0043 0.0040

The average of these values is 0.0023 grm. of Ga_2O_3 per gm. of solution. One part of the salt therefore dissolves in 66.2 cc. of water at 25°, and 100 cc. of the solution contains 1.51 grms. of the alum.

2. In 50 per cent alcohol. 40 cc. of the saturated solution gave a residue that weighed 0.0010 grm., which corresponds to 0.0059 grm. of Ga_2O_3 or 0.0387 grm. of caesium gallium alum per litre of solution. One part of the salt therefore dissolves 25,800 parts of 50 per cent alcohol at 25°, and 100 cc. of the solution contains 0.00387 grm. of the alum.

3. In 70 per cent alcohol. 40 cc. of the saturated solution of the alum gave a residue that weighed 0.0009 grm., which corresponds to 0.0051 grm. of Ga_2O_3 or 0.0356 grm. of caesium gallium alum per litre of solution. One part of

the salt therefore dissolves in 28,000 parts of 70 per cent alcohol at 25°, and 100 cc. of the solution contains 0.00356 grm. of the alum.

4. In a solution containing 35 cc. of water, 50 cc. of absolute alcohol, and 15 cc. of concentrated sulphuric acid. 40 cc. of the saturated solution of the alum yielded 0.0014 grm. of Ga_2O_3 , which corresponds to 0.0350 grm. of Ga_2O_3 or 0.228 grm. of caesium gallium alum per litre of solution. One part of the salt therefore dissolves in 4380 parts of this solution at 25°, and 100 cc. of the solution contains 0.0228 grm. of the alum.

Summary.

1. The spark spectra and the arc spectra of gallium, indium, and zinc have been studied, and the delicacy of the spectroscopic detection of gallium and indium alone and in the presence of each other ascertained. Gallium chloride prepared by double distillation is found to contain less than 0.005 per cent of either indium or zinc.

2. The purification of gallium by fractional electrolysis, and the preparation of pure gallium chloride by distillation are described.

3. Methods for the determination of gallium alone and of gallium, indium, zinc, and aluminium in the presence of one another have been developed.

4. Two new salts of gallium, gallium selenate and caesium gallium selenate alum, have been prepared. The solubilities of ammonium gallium sulphate alum and of caesium gallium sulphate alum in water, in 50 per cent alcohol and in 70 per cent alcohol, have been measured.

MEASUREMENT OF THE THICKNESS OF FILM FORMED ON GLASS AND SAND.*

By EARL PETTIJOHN.

(Concluded from p. 296).

Experimental.—In order to obtain the relationship between surface and amount of liquid to produce sticking, a series of determinations was conducted using the glass pearls, water being used as the titrating liquid. Under these conditions the only variables were those of the solid, including the nature of the surface, the size and the specific gravity of the pearls. For samples from the same source no difference in the nature of the surface was to be expected.

During the whole of this work an attempt was made to find other material suitable for titration and of known surface. Results with this material would permit conclusions to be drawn regarding the capacity of different surfaces to hold liquid films and would thus show the effect of the other variants. No other material was found that could be used in this way.

Reproducibility of Results.—The apparatus as used was subject to some error due to the fact that the quantity of liquid added could only be controlled by opening the lower stopcock of the weight burette. To give an idea of the accuracy obtainable with this apparatus, a series of results obtained with each of two liquids is included. The remaining liquids gave results correspondingly accurate (see Table A).

The per cent error introduced depended principally on the amount of surface titrated or on the amount of liquid added, the greatest variation amounting to from 0.004 to 0.006 grm. of liquid.

The results obtained and the calculations of film thickness are given in Table II.

Discussion of Results.—The liquid required for a titration may be used to form a uniform film of liquid over the surface of the pearls up to the thickness at which flow

* From the *Journal of the American Chemical Society* xli., No. 4.

TABLE II.—Titration Values Using Water.

Sample. Pearls.	Diameter in cm.	Surface sq. cm./grm.	Sp. gr.	Weight.	Titration liquid per grm.	Film thickness.
No. 1.	0.1367	14.67	3.101	0.003988	0.000190	0.0000129
No. 3.	0.1180	17.09	3.090	0.002626	0.000218	0.0000128
No. 5.	0.0808	24.03	3.079	0.000853	0.000303	0.0000126
No. 7.	0.0542	35.46	3.125	0.000261	0.000402	0.0000113
No. 8.	0.0410	46.40	3.069	0.000121	0.000595	0.0000128
No. 9.	0.0540	44.93	2.505	0.000206	0.000297	0.0000066
No. 10.	0.0460	53.14	2.496	0.000122	0.000375	0.0000070
Sands.						
Ottawa	0.0790	28.58	2.656	0.000686	0.000374	0.0000130
10-mesh	0.0494	46.00	2.643	0.000168	0.001310	0.0000285
20-mesh	0.0430	52.28	2.646	0.000110	0.001120	0.0000214
40-mesh	0.0280	81.90	2.650	0.000030	0.001100	0.0000135
60-mesh	0.0170	129.57	2.666	0.000007	0.001480	0.0000114

TABLE III.—Titration Values for Sands and Pearls with Organic Liquids.

Sands.						
Liquids.	10-mesh.		20-mesh.	40 mesh.	60-mesh.	Ottawa.
Nitrobenzene	0.000136		0.000117	0.000109	0.000148	0.00039
Water	0.000133		0.000108	0.000112	0.000151	0.00037
Aniline	0.000122		0.000107	0.000109	0.000148	0.00039
Dimethylaniline	0.000131		0.000108	0.000107	0.000155	0.00039
Phenylodide	0.000126		0.000112	0.000112	0.000149	0.00039
Toluol	0.000134		0.000116	0.000110	0.000146	0.00038
Turpentine	0.000131		0.000116	0.000108	0.000142	0.00039
Pyridine	—		—	0.000109	—	—
Pearls.						
Liquids.	No. 1.	No. 3.	No. 5.	No. 8.	No. 9.	No. 10.
Nitrobenzene	0.00018	0.00020	0.00030	0.00056	0.00027	0.00040
Water	0.00019	0.00022	0.00030	0.00059	0.00030	0.00037
Aniline	—	—	—	0.00055	0.00023	0.00039
Dimethylaniline	0.00017	0.00022	0.00032	0.00059	0.00029	0.00045
Phenylodide	0.00018	—	—	0.00059	0.00030	0.00039
Toluol	—	0.00021	—	0.00053	0.00031	0.00038

would occur. If this is the case a negligible amount of liquid would be required actually to support the grains, this amount being added after the uniform film had been added, and "sticking" would result from a concentration of this added amount at the contact surface of flask and pearl through the action of capillary forces.

In order to determine which of these two hypotheses held or whether the amount used in titrating was the resultant of both effects, some calculations were made of the amount of liquid necessary to support a single grain.

TABLE A.		
Sample	Liquid.	Nitrobenzene.
.. ..	Water.	200 grms.
.. ..		pearls No. 3.
Weight of liquid, grms. ..	0.119	0.040
.. ..	0.119	0.041
.. ..	0.117	0.039
.. ..	0.116	0.042
.. ..	0.120	0.042
.. ..	0.121	0.038
.. ..	0.116	—
.. ..	0.118	—
Average	0.118	0.040
Greatest variation from		
average	0.003 = 2.5 p.c.	5 p.c.
Variation between highest		
and lowest values ..	4.2 p.c.	10 p.c.

On the other hand, the whole amount of liquid required may be necessary to support the pearls through the action of surface tension. In this case no film would form, but all of the liquid added would concentrate at the contact surface, and "sticking" would occur as soon as the surface tension was sufficient to support the pearl.

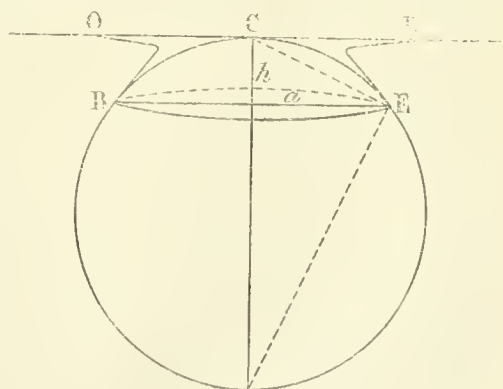


FIG. 2.

Fig. 2 will explain the letters used and the method of calculation followed.

Consider a pearl weighing 0.0001 grm., held to the surface of the flask by surface tension. The liquid holding the pearl may be considered as occupying a volume represented in section by (OBCED), the lowest level of this volume being the circumference of a circle whose radius

is a . Surface tension may be considered as acting along this circumference. If the surface tension and the weight supported by it are known, the length of the circumference required to support the pearl is given $0.0001/\text{sur. ten.}$ Substituting actual values and placing the quotient equal to the circumference of a circle enables one to calculate the value of a in the same units as are used for expressing the surface tension (cm.). Having the value of a , the value of h (thickness of liquid acting) may be calculated, since by geometry—

$$h : a :: a : (R - h),$$

and all of the terms except h are known.

Knowing both a and h , the volume of liquid holding the pearl can be estimated. It was assumed that the volume of liquid necessary to support the pearl would be that required to half fill the volume represented on the figure by (OBED). This is believed to be in excess of the actual amount needed. Calculating this value for the smallest pearl used, one weighing 0.00012 gm. gave 0.0037 cc. per gm. of pearls. Calculating the same value for pearls No. 1, the heaviest pearls used, gave 0.008 cc. per gm. of pearls. These amounts are negligible when the amounts required for a titration are considered. This shows clearly that although the end-point is marked by the appearance of "sticking," which is a surface-tension effect, surface tension itself cannot account for the liquid required for a titration.

The amount of liquid required is directly proportional to the surface, and the film thickness is uniform for the same kind of glass.

As to the actual thickness of film found, it is of the same order as that found by earlier investigators who worked with the vapour phase of water in forming the film. The results are higher than those of all except Parks. It does not seem probable, in view of the results obtained, that there is any difference in the nature of the film itself, whether water in the vapour phase or water in the liquid phase is used to form the film. It also seems probable that what actually takes place on the surface of the grain is a condensation of water vapour. In the titrations in which water was used to form the film it was found that the titrated sample on air drying would again take up the same amount of liquid. It is difficult to see how this could take place repeatedly if a chemical reaction was involved in holding the liquid.

The results obtained with samples No. 9 and No. 10 are only about half as large as those obtained with the rest of the samples. This can only be due to a different surface capacity for holding liquid. The results are close to those obtained by Katz with ornithite, and by Ihmori with glass globes.

Ottawa sand gives the same value for film thickness that the larger series of pearls does. It seems probable that this is a chance agreement, since the surface of the sand differed considerably from that of the pearls both in hardness and in texture.

As a whole, the results indicate that there are two factors which influence the amount of liquid necessary to form the maximum thickness of film. The first factor is the amount of surface, the actual area that the film must cover. The second is the nature of the surface itself, its capacity to hold a film.

Not a great deal is known regarding the variants which determine the capacity factor of a surface. It is probably related to the free energy present in the atoms of the surface layers.

The work up to this point indicated that the film thickness should be independent of the liquid used, providing the liquid is not too viscous to spread readily. It also indicated the desirability of applying the titration method to the determination of the surface of irregular particles like sand grains.

For the purpose of obtaining surface values for the meshed sands complete titrations for each of these samples with water and with each of the organic liquids was carried

out. An attempt was made also to titrate finer sands, 100-mesh, 150-mesh, 200-mesh. These, however, would not permit of an even distribution of the liquid over the surface, and no satisfactory titrations were obtainable.

To determine whether the same thickness of film would be found with a different liquid, titrations were carried out first with the pearls and then with the sands, making use of the organic liquids. The determinations with the pearls were not completed when they were found to check closely for the first liquids used, but those on the sands were completed for all of the liquids.

The organic liquids used were chosen so that the specific gravity, volatility, surface tension, &c., varied.

The results obtained from these two series of titrations are given in Table III., and will be discussed together.

Discussion of Results.—The results show that the thickness of the film is independent of the kind of liquid used for titrating, and that the sand titrations can be checked with as good an accuracy as titrations of pearls. Occasional results vary, but the uniformity for the whole series is pronounced. This proves definitely that the surface tension of the liquid has no effect on the amount of liquid required for a titration. The surface tension of water is much greater than that of the other liquids, but the volume required per gm. is the same. This could not be true if the surface tension influenced the amount of liquid required to produce "sticking."

It also proves that there is no chemical reaction in the ordinary sense of the term when a film of water forms on glass. While it might be possible to imagine such an effect between water and glass, it is obviously impossible to do so with the rest of the liquids of the series. In addition to this the calculated film thickness for different sizes of pearls is found to be the same, showing that the volume for titration varies with the surface.

The definite conclusion can be drawn that these films are not due to the formation of a chemical compound, but that they are held by the free surface energy of the solid. It seems certain that the same force holds a thinner film.

While these films are formed by the addition of liquid to the solid, the inference is that the same conclusion may be drawn for a film formed from the vapour phase. This inference is supported by the fact that the values obtained for the film thickness when formed from the vapour phase are only very slightly lower than those formed by the addition of liquid. It seems probable that a liquid film forms in both cases, but that with the unsaturated vapour phase it never becomes thick enough to show as a normal liquid on the surface of the solid, while when liquid is used the formation of free liquid marks the end of the titration and indicates the thickest film that can form without free liquid being present.

In titrating sands a simple relationship such as was found for the pearl samples does not exist between titrated amount and calculated surface. This is partly due to error in calculating the surface, on the assumption that the grains are spherical, and partly to the fact that extra liquid is required to fill the etchings in the surface. However, if relative effective surfaces are sought they may be expected to be proportional to the titration values, since there is no application of the surface which would not involve the etchings and so produce results which would be proportional to those obtained by the titration method.

Summary.

This paper describes a new method of obtaining the thickness of the maximum film which can form on a surface without free liquid being present. Evidence is presented to show that the liquid forming the film does not combine chemically with the solid. The method has been applied to sand and to glass, and films have been formed with water and with several organic liquids. The film thickness is found to be independent of the liquid used and of the size of the solid particle. The method gives

accurate values for the effective surface of sand particles, providing that surfaces of the same kind are compared.

In conclusion I wish to express my indebtedness to Prof. I. H. Derby for his advice and suggestions in the preparation of this paper.

LEAD IN PHARMACEUTICAL ZINC OXIDE.

By W. D. COLLINS and W. F. CLARKE.

SOON after the outbreak of the present war, difficulty was experienced in obtaining pharmaceutical zinc oxide which would meet the requirements of the United States Pharmacopœia. When the matter was first considered, the statement was made that zinc oxide of the required purity was very easy to obtain. It was even stated that material bought for use as a pigment in painting might be more nearly free from lead than a certain sample of pharmaceutical zinc oxide which contained about 0.2 per cent of lead.

Mr. C. L. Black, of the Philadelphia Station of the Bureau of Chemistry, reported in May, 1917, that analysis of such samples of zinc oxide as could be procured on the market at that time indicated that practically all the zinc oxide obtainable contained more lead than was permitted by the U.S.P. test. Some manufacturers at this time stated on the labels that the zinc oxide sold by them contained heavy metals slightly in excess of the U.S.P. limit. Prof. C. H. La Wall published an article calling attention to this matter, and made the suggestion that all samples of pharmaceutical zinc oxide should be tested for lead. (*Am. Journ. Pharm.*, 1917, lxxxix., 353. In a later article (*Ibid.*, 1918, xc., 499) Prof. Le Wall notes that U.S.P. zinc oxide is now on the market. He proposes tests for lead which will detect 0.03 per cent PbO in zinc oxide, while the present U.S.P. test under the best conditions will detect 0.05 per cent).

In order to learn whether it would be possible to obtain zinc oxide reasonably free from lead, samples were obtained on the market and from manufacturers, and the question was taken up with the U.S. Geological Survey, and with manufacturers of zinc oxide. It was learned from Mr. C. E. Siebenthal, of the U.S. Geological Survey, that one company producing zinc in the United States owned a mine which contained no lead minerals, and therefore should be able to produce zinc oxide free from lead. It would seem probable that zinc oxide made from electrolytic zinc should be free from lead. It was learned from manufacturers that zinc oxide was being made according to both of these principles, and that the products contained much less lead than the amount necessary to respond to the U.S.P. test for heavy metals.

Test for Lead in Zinc Oxide by the U.S.P. Test for Heavy Metals.

In order to determine the sensitiveness of the U.S.P. test for lead in zinc oxide two series of experiments were conducted entirely independently in order to establish the limits of sensitiveness. Different quantities of lead from a solution of lead nitrate were made up with zinc oxide and hydrochloric acid so as to give the concentrations of zinc and acid prescribed by the U.S.P. for the test for heavy metals. In one series of tests (W.F.C.) the hydrogen sulphide used was made according to the directions of the Pharmacopœia. In the other series of tests (W.D.C.) the hydrogen sulphide used was prepared in the ordinary manner by the use of hydrochloric acid and ferrous sulphide and the gas was washed through water. No difference could be detected in the results by the two methods.

It was found that a sample of zinc oxide might contain as much as 0.05 per cent lead and fail to respond to the test for heavy metals. In some cases the test would be obtained and in others it would fail. When the sample

contained as much as 0.1 per cent a positive test was always obtained, and with any amount greater than 0.05 per cent there was rarely any doubt about the response to the test.

Samples.

A number of samples of zinc oxide were purchased at various drug stores. Some samples were furnished by manufacturers and others were obtained from dealers through the regular purchasing office of the Bureau.

TABLE 1.—Zinc Oxide.

Sample No.	Received.	Dealer.	Producer or manufacturer.	Lead, per cent.	U.S.P. test.
117 (a)	1-13-17	A	?	0.25	+
118 (a)	1-16-17	B	C	0.036	0
119 (a)	1-16-17	A	?	0.25	+
133 (a)	8-4-17	D	E	0.19	—
134 (a)	8-4-17	F	G	0.19	+
137 (a)	8-6-17	B	C	0.26	+
130 (b)	1915	H	H	0.041	0
148 (c)	9-27-17	I	I	0.006	0
158 (d)	11-28-17	I	I	0.004	0
159 (d)	11-29-17	I	I	0.008	0
155 (e)	11-5-17	C	K	0.013	0
178 (e)	2-1-18	H	I	0.004	0
187 (e)	2-4-18	L	I	0.008	0
<i>Metallic Zinc.</i>					
149 (f)	1914	—	M	0.026	—
145 (g)	1917	N	M probably	0.094	—
146 (h)	9-26-17	—	K	0.012	—
<i>Pigment Zinc Oxide.</i>					
135 (i)	8-4-17	O	—	0.13	Trace
136	8-4-17	P	—	53.2	Heavy

- (a) Purchased at local drug store.
- (b) From Bureau stock of reagents.
- (c) Show sample from office of manufacturer.
- (d) Sample sent by manufacturer.
- (e) Purchased by Bureau Supply Office.
- (f) Analysis on label, lead 0.01 per cent.
- (g) Analysis on label, lead none.
- (h) Sample furnished by manufacturer.
- (i) About 22 per cent barium sulphate.

Samples of zinc oxide were also purchased at two paint stores. A few samples of metallic zinc were examined for their content of lead.

Method of Analysis.

Lead was determined by the well known method of separating as sulphate and weighing as chromate. From 5 to 40 grms. of zinc oxide or zinc were dissolved in water and sulphuric acid, with a slight excess of acid. The volume was usually about 100 cc. for 10 grms. of zinc oxide. Alcohol (95 per cent) was added in quantity just short of that necessary to start precipitation of the zinc sulphate, usually making about one-third of the final volume. The solution was allowed to stand overnight; the lead sulphate was filtered off on asbestos, washed with 50 per cent alcohol, and dissolved in ammonium acetate. The lead was reprecipitated as chromate, after acidifying with acetic acid, by adding potassium dichromate solution. After standing overnight the lead chromate was filtered on asbestos in a weighed Gooch crucible, dried to constant weight at 110°, and weighed. The accompanying table gives descriptions of the samples and the results obtained for lead, and also the results of testing according to the United States Pharmacopœia.

Summary.

For a short time after the beginning of the war it was not possible to procure zinc oxide of the U.S.P. standard produced in the United States.

The U.S.P. test for heavy metals will not detect less than 0.05 per cent of lead in zinc oxide.

It is possible at the present time to obtain zinc oxide which, with respect to the presence of lead, is of much higher quality than is called for by the requirements of the U.S.P. — *Journal of Industrial and Engineering Chemistry*, ii., No. 2.

BOARD OF TRADE ANNOUNCEMENTS.

THE Board of Trade are in receipt of information from the Foreign Office that the Danish Government have now given a general guarantee, which has been accepted by the Associated Governments, that goods imported into that country will not be re-exported to enemy countries. They announce therefore that, except for goods on Lists A or B, all restrictions on export to Denmark, whether by freight or by parcel post, have been removed.

Exporters should, however, satisfy themselves that the goods are not subject to any Danish import prohibition.

Applications for licences to export goods on Lists A or B should continue to be made to the Export Licence Department (4, Central Buildings, Westminster, S.W. 1), but no certificates from the Danish Associations need be produced.

IMPORT OF DYESTUFFS.

By the Proclamation of February 24, 1919, the importation into the United Kingdom of the following products was prohibited except under licence, viz. :—

All derivatives of coal-tar generally known as intermediate products capable of being used or adapted for use as dyestuffs, or of being modified or further manufactured into dyestuffs.

All direct cotton colours, all union colours, all acid wool colours, all chrome and mordant colours, all alizarine colours, all basic colours, all sulphide colours, all vat colours (including synthetic indigo), all oil, spirit, and wax colours, all lake colours, and any other synthetic colours, dyes, stains, colour acids, colour bases, colour lakes, leuco acids, leuco bases, whether in paste, powder, solution, or any other form.

At the same time, in accordance with the arrangements outlined in a White Paper issued some months ago (Cd. 9794) setting out the Government scheme for affording State assistance to the dye-making industry, a special Committee, known as the Trade and Licensing Sub-Committee, was established with offices at Danlce Buildings, 53, Spring Gardens, Manchester, in order to determine the kinds and quantities of the dyestuffs which were to be licenced for import and generally to deal with all questions relating to such importation.

This Sub-Committee consists of Dr. A. Ree and Mr. J. Turner (representing the dye manufacturing industry) and Mr. W. E. Kay and Mr. Thorp Whitaker (representing the dye using industry), with Mr. W. Graham of the Board of Trade as Secretary.

In order that there should be no undue delay in dealing with applications to import dyestuffs during the first few weeks whilst the necessary organisation was being set up, the Committee issued a General Licence permitting the importation of all dyestuffs of *bona fide* American, French, or Swiss origin, but this concession was withdrawn on April 9, and since that date licences have been necessary for the import of all consignments of dyestuffs coming into this country whatever their origin.

Whilst the regulation of the import of dyestuffs was primarily necessitated in order to prevent the free access of German materials to this market it was felt that some measure of control was desirable over all imports if the scheme was to be thoroughly effective. It was therefore decided that a Central Importing Agency should be established under the direct control of the Committee through

which all imports of dyestuffs must pass at some stage. As soon as the Committee are in a position to consider applications for the import of German dyestuffs, which will not be until after the withdrawal of the Trading with the Enemy Regulations, the Central Importing Agency will be the medium through which supplies are made available to consumers. Except in the case of German dyes, the Agency will now undertake if desired the purchase of dyestuffs abroad on behalf of consumers, but where it is desired to make purchases direct or through recognised merchants the goods will merely require to be consigned to the Agency for the account of the particular consignee and the shipping documents made out accordingly. For its services the Agency will charge a commission of 1 per cent on the invoice value of the goods with a minimum charge of 5s., but this charge will not, of course, include any incidental expenses such as freight, insurance, storage, &c., which must naturally be additional and borne by the importer. The Offices of the Central Importing Agency for the time being are at 21, Spring Gardens, Manchester.

Any firms desiring further information on the subject or wishing to make application for an import licence are advised to communicate direct with the Secretary of the Licensing Sub-Committee, at the address already given (53, Spring Gardens, Manchester).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 5, 1919.

Sir J. J. THOMSON, O.M., President, in the Chair.

THE following papers were read :—

"The Relation between the Refractivity and Density of Carbon Dioxide." By P. PHILLIPS, D.Sc.

"On the Colours of the Striae in Mica, and the Radiation from Laminar Diffracting Boundaries." By P. N. GHOSH.

(a) The striae are shown by an examination of the Haidinger's rings in mica (and otherwise) to be the boundaries between parts having slightly different thicknesses.

(b) The colour of any stria as seen in the Foucault test is complementary to the colour of the central fringe in the laminary diffraction-pattern produced by it.

(c) The colours are altered by holding the mica obliquely, or by immersing it in a cell containing liquid.

(d) The luminosity of a stria in the Foucault test is approximately a maximum when the phases of the wave-front, after passing through the plate on the two sides of the stria, are opposite, and practically zero when the phases are identical.

(e) Attempts to reproduce the phenomenon by etching glass plates with dilute hydrofluoric acid were not very successful, owing, apparently, to a want of sufficient sharpness in the boundary thus produced. This is indicated by the fact that such a plate shows distinct *asymmetry* with reference to the direction of the incident light, both in the Foucault test and in laminar diffraction.

(f) The striae in mica appear doubled (with a black line in the centre) when the light coming to a focus is screened in a symmetrical manner, instead of by a knife-edge, as in the Foucault test.

"A Study of the Catalytic Actions at Solid Surfaces." By E. F. ARMSTRONG, D.Sc., and T. P. HILDITCH, D.Sc.

The rate of hydrogenation of a number of unsaturated fatty oils in presence of finely disseminated nickel has been studied and the results expressed in the form of curves. These are characterised by an initial linear segment followed by an abrupt change of direction to a segment of gentler slope, which is also linear at first, but

subsequently may exhibit considerable curvature. The point of inflexion is at a corresponding part of each curve. The two well-defined linear components of the curves correspond to the hydrogenation of glycerides more unsaturated than olein and to the hydrogenation of olein. The curves never approach the logarithmic type required for a unimolecular action.

The general aspect of the curves obtained for catalytic hydrogenation is markedly similar to those obtained in the case of enzymes, and they undoubtedly represent related phenomena. In each the catalyst (enzyme or reduced nickel) unites primarily with the organic compound about to undergo change (hydrolyte or unsaturated glyceride), the complex so formed being decomposed by the other component of the interaction (water or hydrogen). In each case, moreover, action takes place entirely at the surface of colloid particles, and activity of catalyst depends entirely on production of maximum surface and avoidance of impurities likely to destroy or dirty this surface.

It is considered that the interchanges take place in an electrolytic circuit in which the interacting substances are necessarily all comprised. Hydrogen and fatty oil are both to be thought of as coupled with nickel and interaction as brought about through inclusion in the system of the electrolyte required to establish a conducting circuit. Both hydrogen and fatty oil are to be regarded as having some affinity for the catalyst, and the rate of change is to be considered as determined by the rate at which the less active (hydrogen) enters into productive association with the catalyst.

OBITUARY

SIR BOVERTON REDWOOD.

THE death of Sir Boverton Redwood, Bart., which took place on June 4 last, has deprived science and chemistry in particular of one of its most active workers.

Sir Boverton was born in April, 1846, and was therefore in his seventy-fourth year. Since the age of twenty-three, when he was appointed Secretary to the Petroleum Association, he has been an active and prominent man in the chemical world. He has served on many commissions connected with the Petroleum industry, and during the war gave much assistance to the Admiralty and other bodies.

His only son, Bernard Boverton, died in 1911, and his grandson, Thomas Boverton, born in 1906, succeeds to the baronetcy.

CORRESPONDENCE.

THE DISRUPTION OF THE NITROGEN ATOM.

To the Editor of the Chemical News.

SIR,—In the fourth paper of a series entitled "Collisions of α -Particles with Light Atoms," by Sir E. Rutherford (Papers I. to V., *Phil. Mag.*, June, 1919, pp. 537—587), there is an announcement that is somewhat sensational, and with your permission I will give a short account of the subject supplemented by the author's discussion of the results.

The nuclear theory of the atom indicates the possibility of impressing on the nuclei of light atoms a swift translatory motion by the impact of α -particles thereon and in the case of bombarding hydrogen the H atom should acquire a velocity 1.6 times that of the α -particle when receiving therefrom a direct blow, whilst the energy acquired by the H atom should be 0.64 of the energy of the α -particle.

Prof. Marsden detected scintillations on a zinc sulphide screen, placed upon the range of the α -particles, due to the presence of high-speed H atoms when the α -particles were passed through gaseous hydrogen, the speed of the H atoms being considerably greater than that of the α -particles before impact; their range of projection under certain conditions is over 100 cm. in hydrogen, which is four times the movement of colliding α -particles in the same gas. Moreover, this range is in agreement with that calculated by Darwin from Bohr's theory of absorption of α -particles by matter. It was noted that the number of hydrogen scintillations was in all cases too great to be accounted for by the presence of hydrogen in the radio-active material used or at the source of the α -particles.

It was considered probable that besides the H atoms being driven in a definite direction, O and N atoms from the air were similarly given a high velocity, and it was found that these atoms produced scintillations on the screen, but in the absence of hydrogen scintillations appeared evidently due to hydrogen disrupted from the nitrogen by the force of the α -particle impacts. In regard to the experimental details given, with dried air the scintillations increased in number. While the scintillations were observed with air and oxygen no anomalous effect (see discussion below) was observed either with oxygen or carbon dioxide, and the comparative effect observed with chemically pure nitrogen indicates that the source of the effect, presumably due to the dismemberment of the nitrogen atom, arises from the nitrogen itself. The removal of dust from dry air did not appreciably reduce the effect. It was found that the scintillations varied with the air pressure in the vessel, as should be expected if they arise from the impacts of α -particles on the gases present. The presence of H atoms was indirectly confirmed by obtaining deflections in magnetic and electrostatic fields, but "in order to settle this question definitely it will probably be necessary to employ a solid nitrogen compound free from hydrogen as a source and use much stronger sources of α -rays."

It is of interest to note that for every 109 collisions with the hydrogen molecules only one α -particle passes close enough to the nucleus to give rise to a swift H atom.

After detailing a series of analytical experiments, touched upon above, which brought to light the apparent disruption or dismemberment of the nitrogen atom, Sir E. Rutherford concludes with the following discussion of the results:—

"From the results so far obtained it is difficult to avoid the conclusion that the long range atoms arising from collision of α -particles with nitrogen are not nitrogen atoms but probably atoms of hydrogen, or atoms of mass 2. If this be the case, we must conclude that the nitrogen atom is disintegrated under the intense forces developed in a close collision with a swift α -particle, and that the hydrogen atom which is liberated formed a constituent part of the nitrogen nucleus. We have drawn attention in Paper III. to the rather surprising observation that the range of the nitrogen atoms in air is about the same as the oxygen atoms, although we should expect a difference of about 19 per cent. If in collisions which give rise to swift nitrogen atoms, the hydrogen is at the same time disrupted, such a difference might be accounted for, for the energy is then shared between two systems. It is of interest to note, that while the majority of the light atoms, as is well known, have atomic weights represented by $4n$ or $4n+3$, where n is a whole number, nitrogen is the only atom which is expressed by $4n+2$. We should anticipate from radio active data that the nitrogen nucleus consists of three helium nuclei each of atomic mass 4, and either two hydrogen nuclei or one of mass 2. If the H nuclei were outriders of the main system of mass 12, the number of close collisions with the bound H nuclei would be less than if the latter were free, for the α -particle in a collision comes under the combined field of the H nucleus and of the central mass. Under such conditions it is to be expected that the α -particle would only occasionally approach close

enough to the H nucleus to give it the maximum velocity, although in many cases it may give it sufficient energy to break its bond with the central mass. Such a point of view would explain why the number of swift H atoms from nitrogen is less than the corresponding number in free hydrogen and less also than the number of swift nitrogen atoms. The general results indicate that the H nuclei, which are released, are distant about twice the diameter of the electron (7×10^{-13} cm.) from the centre of the main atom. Without a knowledge of the laws of force at such small distances it is difficult to estimate the energy required to free the H nucleus or to calculate the maximum velocity that can be given to the escaping H atom. It is not to be expected, *a priori*, that the velocity or range of the H atom released from the nitrogen atom should be identical with that due to a collision in free hydrogen.

"Taking into account the great energy of the motion of the α -particle expelled from radium C, the close collision of such an α -particle with a light atom seems to be the most likely agency to promote the disruption of the latter; for the forces on the nuclei arising from such collisions appear to be greater than can be produced by any other agency at present available. Considering the enormous intensity of the forces brought into play, it is not so much a matter of surprise that the nitrogen atom should suffer disintegration as that the α -particle itself escapes disruption into its constituents."

Further developments will no doubt be awaited with interest.—I am, &c.,

F. H. LORING.

June, 1919.

NOTES.

GLUE.—A good sterile glue can be made by taking—Glue, 50; water, 50; glycerin, 2; calcium chloride, 2; thymol, 1. Melt and use hot.

THE Annual Report of the British Science Guild was presented by Sir Richard Gregory at a meeting held in the Goldsmiths' Hall on June 17. The chair was occupied by Lord Sydenham, who, at the conclusion of the Official business, gave an address on "Science and Labour Unrest." His Lordship suggested that the labour unrest, so manifest at the present time, is due to the triumphs of applied science, and also that science in its broadest aspect can provide the remedies and secure industrial peace. In a broad sketch commencing with Primitive man and the means he had to employ to enable him to maintain his existence, and ending with the present day mechanic, he showed how science by the recognition of principles and the invention of appliances to minimise manual exertion, has completely changed the character of labour, at all events of the educated European. The advantages and evils of trade unions were discussed, and the immediate need for grappling with the housing problem and the bettering of the conditions of the working classes was pointed out. In conclusion Lord Sydenham insists that every manual worker must honestly put forward his full effort within the agreed hours of labour, and there must be no idlers in this country. "There can be no room for them in the strenuous times which we must face. Knowledge we now have in abundance. Our future existence as a nation and an Empire depends upon whether we have wisdom in all classes. Science, which has unconsciously caused some of the evils which we must remove, can now point the way to the restoration of national prosperity. Education, which—imperfectly assimilated and sometimes ill-directed—has contributed to the ferment of wild ideas from which the world is now suffering, may in time be able to implant an understanding of the fundamental laws of national and industrial economics. It will at least increase the flow from the

ranks of manual labour to that of brain work, which is now far more than ever important to industrial and commercial progress." At the conclusion of the address Sir J. J. Thomson in a brief speech referred to the activity of scientific research during the war, and pointed out the necessity for scientific education for all classes, but particularly for those who took a prominent part in the affairs of men. He also drew attention to the changes that were being made in the examination system, from which good results could be expected.

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